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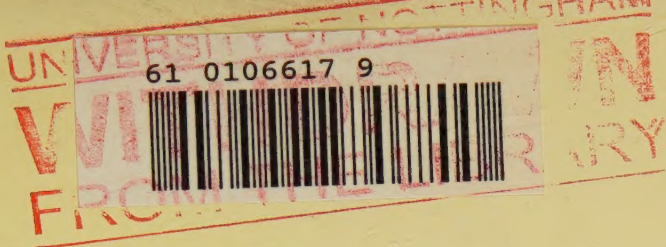
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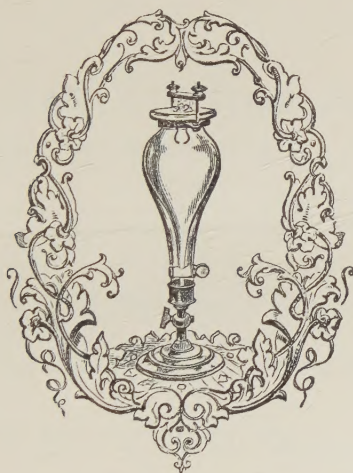
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ELEMENTS  
OF  
CHEMICAL AND PHYSICAL  
GEOLOGY.

BY  
GUSTAV BISCHOF, PH. D.

PROFESSOR OF CHEMISTRY AND TECHNOLOGY IN THE UNIVERSITY OF BONN.

TRANSLATED FROM THE MANUSCRIPT OF THE AUTHOR, BY

BENJAMIN H. PAUL, F.C.S.,

AND

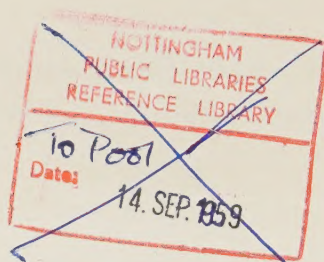
J. DRUMMOND, M.D.

VOL. I.

LONDON:  
PRINTED FOR THE CAVENDISH SOCIETY,  
BY HARRISON & SONS, ST. MARTIN'S LANE.  
1854.



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## INTRODUCTORY REMARKS.

THE German edition of my work on Chemical and Physical Geology, of which the first volume appeared in 1847, the second in the following years in six parts, and of which the seventh and last part will appear in a few weeks, had the good fortune to attract the notice of the Cavendish Society (Report of the fourth anniversary meeting of this Society). They wished an English translation of that work so condensed as not to exceed 1500 pages, the German edition containing about 3300 pages. In the work which I have accordingly supplied I have chosen a different, and as appears to me, more systematic arrangement of the chapters than in the German edition. Allied subjects are brought closer to one another, and in this way space has been spared. The present edition, indeed, is by no means a mere translation or abridgement of the German, but an independent work, in which the chemico-geological facts ascertained since the preparation of the latter, have been taken up so far as space permitted.

The laws of combination in the mineral kingdom, which I have been gradually discovering during the preparation of the German edition, are collected into Chapter I. A few new laws discovered since this chapter was sent to the press will be considered in the second volume. It is to be desired that other chemists would give their attention to this subject; experiments, as simple as nature is in her operations, will then lead to a more and more intimate knowledge of laws of combination—only in this way can we arrive at the correct explanation of the manifold processes of decomposition, conversion, and formation

of minerals and rocks going on in the mineral kingdom. The Plutonic explanations, founded frequently on untenable hypotheses, will then retire more and more into the background, and at length vanish entirely out of science.

The incomparable aids to the investigation of the laws of combination, the pseudomorphs, by a knowledge of which Blum, Breithaupt Haidinger, G. Rose, and other mineralogists, have rendered invaluable services to geology, are considered in Chapter II. The pseudomorphs constitute the storehouse, out of which the knowledge of the laws of combination is chiefly to be drawn; for by the pseudomorphs is the chemist taught what has taken place—it remains for him to ascertain how it has taken place.

The waters on our earth, the springs, rivers, lakes, and seas, by and in which the greatest part of its surface, so far as we can observe, has been formed or altered; the sediments thrown down from these waters in the mechanical and chemical ways, as well as by organic agency, have been treated in the following chapters. The knowledge of the substances partly suspended, partly dissolved in water, explains not only the formation of these sediments, but it leads also to a correct notion of the manifold processes which have taken place and still take place in rocks permeated by water. This knowledge is therefore the chief foundation on which chemical geology rests, for just as the greater part of the present crust of the earth has been deposited from water, so, as I shall endeavour to shew, the metamorphic rocks, derived from sedimentary formations, have also been changed by the aid of water.

Among the most important of the substances contained in water, which are constantly effecting changes in rocks, are carbonic acid and oxygen. The meteoric waters derive them from the atmosphere and convey them into the rocks. It is known that the constituents of the atmosphere are exposed to constant change by the agency of the respiration of animals, the vegetation of plants, and the putrefaction of all organic substances. The constituents of rocks likewise take a share in this change: the oxygen and the carbonic acid which they have obtained from the atmosphere return, under certain circumstances, into it again. The atmospheric air, therefore, is of



the highest importance for the chemical processes in the mineral kingdom; hence the consideration of it could not be omitted in chemical geology.

The share which the mineral kingdom takes in the change of the constituents of atmospheric air, is shown by exhalations of gases from the interior of the earth; the most extensive of these exhalations is that of carbonic acid gas. Observations and experiments, which I had an opportunity of instituting on this remarkable phenomenon over a long period of years, placed me in a position to treat of it somewhat fully, and to indicate processes to which it possibly owes its origin. The mutual action between the constituents of atmospheric air, and the organic as well as the inorganic substances of the three kingdoms of nature, led to the question of the origin of carbon. Its occurrence in the diamond, anthracite, and graphite, in coal, and in other combustible products of the mineral kingdom, as well as in exhalations of carburetted hydrogen gas; the formation of these substances, and their relation to inorganic bodies, form the subject of several chapters.

The exhalations of sulphuretted hydrogen which, considered in relation to their frequency and quantity, no doubt play a very subordinate part compared with the exhalations of carbonic acid, are, however, no less important phenomena than the latter, for they furnish those acids of sulphur (sulphurous and sulphuric acids), which exist in the free state in the mineral kingdom; and what is still more important, the native sulphur. All facts bearing on this subject, as well as results deducible from it, are collected into a single chapter.

The later chapters are devoted to the consideration of the simple salts occurring in the mineral kingdom; according to the extent of their distribution and importance, more or less space was assigned to them. Rock-salt, sulphates, and carbonates occupy the first rank in these respects. The occurrence of rock-salt, the already frequently attempted explanation of its formation; the occurrence of chloride of sodium in the sea, in salt lakes and springs,—all this required a full explanation, rendering it necessary that a special chapter should be devoted to it.

Mr. Paul translated chapters I to VI, VIII to XIII, XV,

and XVI. Dr. Drummond translated chapters VII, XIV, XVII to XIX. Several additions which I subsequently made to the chapters translated by Mr. Paul, especially VIII, IX, XIII, XV, and XVI, were in like manner translated by Dr. Drummond. I have examined these translations with every care, and have corrected them wherever the sense was not quite attained; they therefore perfectly agree with my manuscript. As I have read the last proof sheets I can certify that the press is also correct, particularly as regards the proper names.

The two translators of the first volume of my work, I feel myself bound to thank. Dr. Drummond continued the translation, after Mr. Paul, with great willingness and sacrifice of time, which deserves acknowledgment the more, as chemical geology lay somewhat remote from his own studies.

GUSTAV BISCHOF.

Bonn, *June*, 1854.

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## CHAPTER I.

### LAWS OF COMBINATION IN THE MINERAL KINGDOM.

THE analysis of any spring water whatever is sufficient to show that rain, in penetrating through rocks, takes up mineral substances. Among these are found some which would be dissolved on treating the material of the rock with water, and which, consequently, exist as such in the rocks. But we find also other compounds which do not exist as such in the rocks. The latter include the alkaline carbonates, which never occur in rocks, and, when the springs issue from rocks consisting only of silicates, the carbonates of lime, magnesia, protoxide of iron, and protoxide of manganese.

All these substances are present in great abundance in spring water, rich in carbonic acid. There can, therefore, be no question that their quantity is determined by the amount of carbonic acid, and that fresh water contains only small quantities of these carbonates on account of the minute quantity of carbonic acid present, which is derived partly from the atmosphere and partly from vegetable mould.

The principal constituents of all rocks, with the exception of limestone, dolomite and gypsum, are silicates of alumina, lime, magnesia, protoxides of iron and manganese. We know that even weak acids are able to decompose these silicates, when their silica exists in the soluble modification. But even those silicates, in which the silica exists in its insoluble modification, are unable to resist the long-continued action of acids.\*

With the exception of some rare instances, we are unacquainted with any other acid existing in the water penetrating through rocks

\* It will be seen in Chapter VIII. that silica may pass from its insoluble into its soluble modification in consequence of a greater degree of mechanical subdivision.



than the carbonic. It is, therefore, to this that we must ascribe the gradual decomposition of rocks, the products of which are the carbonates we find in spring water.

The alkaline carbonates decompose a great number of salts. But their behaviour towards the silicates, of which rocks consist, has not yet been investigated. If they decompose silicates, it would be allowable to suppose that water after having, by means of its free carbonic acid, converted a certain quantity of alkaline silicates into carbonates, and dissolved the latter, would be capable, during its further penetration into the rock, of decomposing other silicates.

The behaviour of the bicarbonates of lime and magnesia, in solution, towards other salts, and especially silicates, is likewise still uninvestigated.

The above remarks show what kind of chemical facts are required to form the ground-work of a knowledge of the various processes of alteration and decomposition going on in the mineral masses, constituting the surface of the globe. From investigations of this kind the following empirical laws have been derived:—

1. The silicates of alkalies, alkaline earths, protoxides of iron and manganese, are decomposed by carbonic acid at ordinary temperatures.

a. On passing a current of carbonic acid through a solution of silicate of potash or soda, silicic acid is not precipitated at first, and after twenty-four hours only a very insignificant turbidity is perceptible. The solution contains much carbonate of potassa, but no bicarbonate. In this action a considerable quantity of silicate is decomposed and a supersilicate formed.

This experiment leads to the important result that alkaline carbonates and silicates can exist together in solution, it being immaterial whether the water contains only the small quantity of carbonic acid derived from the atmosphere and vegetable mould, or the larger quantity proper to acidulous springs.

b. On passing a current of carbonic acid through water, in which silicate of lime is suspended, a sediment is formed, which effervesces with acids, and silica is separated in flocks. If carbonic acid is passed through a *solution* of silicate of lime, no precipitate is formed, because carbonate of lime is more soluble than the silicate.

c. Carbonate of magnesia, being likewise much more soluble than the silicate artificially prepared, a solution of the latter is not rendered turbid by carbonic acid. But if the solution after

having been treated with carbonic acid is evaporated to dryness, the residue effervesces with acids. Silicate of magnesia, however, is not decomposed by carbonic acid when merely suspended in water. Natural silicate of magnesia (steatite), finely powdered, suspended in water and treated with carbonic acid for twenty-four hours does not show the slightest effervescence with acids. When the filtered liquid is evaporated to dryness there remains a black residue amounting to  $\frac{1}{1609.41}$  of its weight. This also does not effervesce with acids. In the experiment made, the quantity was too small to examine quantitatively, but it was found to contain silica and peroxide of iron, with a small quantity of magnesia. The carbonated water appears, therefore, to have dissolved silicates of these bases. But it cannot under any circumstances decompose steatite. The decomposition of the artificial silicate of magnesia, when in solution, is owing to the silica being in the soluble modification, while in steatite it is in the insoluble modification, which is not acted upon even by the strongest acids.

This very different behaviour towards carbonic acid of the otherwise analogous earths, lime and magnesia, in their combinations with silica, is, as we shall subsequently see, of great geological importance. It affords an explanation of the ready disintegration of rocks containing silicate of lime, and the extreme durability of those containing silicate of magnesia. It moreover explains why steatite and talc, consisting in their purest form only of silicate of magnesia, are among the most unalterable minerals.

With regard to acidulous waters, it must be remarked, that on account of their occurring only in a few places, they are of much less importance in the consideration of the changes which take place in rocks, than the meteoric water which filters through rocks. Since this fresh water usually contains only a small quantity of carbonic acid, a decomposing action by this acid on the silicates of lime and magnesia in these waters can take place only after the lapse of a considerable time.

*d.* The decomposition of protosilicates of iron by carbonic acid cannot well be determined experimentally, on account of the difficulty of preparing them in a state of purity. Since, however, there is scarcely a spring the water of which does not contain at least traces of protocarbonate of iron, even when issuing from rocks which do not contain this substance, but only protosilicate, not the least doubt can exist that the protocarbonate originates in the decomposition of this silicate by the carbonic acid of the water. The protocarbonate of iron occurring in the drusy cavities of

rocks which, like basalt, contain nearly always protosilicate only, can be formed only by such means.

As carbonic acid does not combine with peroxide of iron, it cannot decompose persilicates of iron. The protocarbonate of iron in spring waters and in drusy cavities therefore can only originate from the protosilicate, unless peroxide of iron has been converted into protoxide by reduction.

The presence of protosilicates of iron in waters, even when they contain free carbonic acid, may with good reason be conjectured. For since these silicates are decomposed with great difficulty, even by boiling hydrochloric acid, it is to be expected that they may co-exist in solution with carbonic acid, without suffering any perceptible decomposition. This conjecture is fully confirmed by the presence of silica in the iron ochre deposited by carbonated springs. This silicic acid cannot exist in the water in a free state, for I have frequently observed that on treating such ochres with hydrochloric acid, a brownish residue of silica remains, which does not become white until it has been long boiled with the acid. If this silica were not chemically combined with the peroxide of iron, this would readily be dissolved.

Kersten\* found protosilicate of iron in the ochre deposited at the carbonated springs of Marienbad in Bohemia. Rammelsberg† remarked that the ochre deposited by the water of an adit gelatinized with acids. Kosman‡ likewise found protosilicates of iron and manganese in the mineral water of Niederbronn. The solubility of protosilicate of iron in carbonated water is also shewn by the previous experiment. (1 c.)

With regard to the occurrence of silica in brown ochre beds, it ought to be remarked that the hydrated peroxide of iron is the first constituent which is precipitated from chalybeate waters by the oxidizing action of the atmosphere. The silica, however, is deposited only on evaporation. But, as in the instances above-mentioned, silica is deposited together with peroxide of iron, there can be no doubt that they are chemically combined.

It is certain that the brown ochre deposited by chalybeate waters existed in them for the most part as protocarbonate, but it cannot be decided whether the persilicate found in these ochres existed in the water, as such, or as protosilicate. If, however, the iron was combined with silica in the form of peroxide, it does not

\* Neues Jahrbuch für Mineralogie, etc. 1845, p. 659.

† Poggendorff's Ann. T. 72, p. 574.

‡ Journ. de Pharm. et de Chimie. 3 Sér. T. 16, p. 43.

appear why it should be deposited together with the hydrated peroxide. The oxidizing action, in virtue of which the protocarbonate is decomposed, and peroxide deposited, cannot take place when the iron is already combined as peroxide with silica. For this reason it is probable, that protosilicate of iron alone exists, in solution, in chalybeate waters, and that the persilicate, formed by oxidation, is deposited because it is more sparingly soluble than the former.

*e.* It is highly probable that all which obtains with regard to the decomposition of protosilicate of iron by carbonic acid, and its occurrence in spring waters, may also be assumed of the decomposition of the protosilicates of manganese.

*f.* As carbonic acid does not combine with alumina, it is evident that silicate of alumina cannot be decomposed by this acid.

The presence of protosilicates of iron and manganese in spring waters having been proved, it only remains to show that these waters may also contain silicates of lime and magnesia.

Pagenstecher and Müller\* have found that the direct determination of the carbonic acid, in the spring and well-waters of Berne, gives a quantity less than would be found if the lime were present entirely as carbonate. These chemists are, therefore, of opinion that a small quantity of this earth is combined with silica. Löwig seems to have observed the same fact in his analysis of the thermal spring of Pfäfers.

In analysing mineral waters, I have always found that the magnesia separated from them does contain a small quantity of silica. As magnesia has a great affinity for silica, and of all the other bases contained in these waters, forms the most sparingly soluble compound with it, there is great probability that a real silicate of magnesia is separated in the analysis. According to Berzelius† silicate of magnesia is likewise separated on evaporating the hot water of Carlsbad. Kersten‡ has found silicates of lime and magnesia in the mineral waters of Marienbad (Kreuz- and Ferdinandbrunnen), which are rich in carbonic acid. On evaporating these waters, either at ordinary or elevated temperatures, carbonates of lime and magnesia are first deposited, and then silicates, becoming gelatinous with acids.

The silicates which are found in spring waters may either be

\* Mittheilungen der naturforschenden Gesellschaft in Bern. 1844. No. 31-33, p. 152.

† Gilbert's Annal. der Physik. T. 74, p. 141.

‡ Loc. cit., p. 659.



dissolved, as such, from the rocks, or they were formed by the reciprocal action of their constituents and those of the water, as has been proved possible by the above investigations.

2. Silicates, in which the silica exists in its soluble modification, are decomposed in the wet way by the stronger acids. Seeing, however, that sulphurous acid, sulphuric acid, and hydrochloric acid make their appearance naturally, only during volcanic eruptions, such decompositions must play a merely subordinate part. But as exhalations of sulphuretted hydrogen take place, not merely from volcanos, but are generally distributed, and since the sulphuretted hydrogen gives rise, in contact with the air, to the formation of sulphuric acid, it is obvious, that in this way decompositions of silicates may take place on a large scale.

Thus Sauvage\* found in tertiary rocks of the island of Milo, considerable quantities of alum-stone, and from 3·8 to 31·6% of gelatinous silica. He regards these substances as products of the decomposition of rocks containing felspar effected by sulphuric acid, traces of which are still to be found in the rocks. This sulphuric acid unquestionably proceeds only from sulphuretted hydrogen exhalations, the former existence of which is likewise indicated by the sulphur, which is distributed all over the island.†

In the department of the Ardennes, in the so-called Gaize, a formation three hundred feet in thickness, extraordinarily fissured, and underlying the chalk, the same chemist‡ found 56% of gelatinous silicic acid, and 17% of fine quartz-sand. It is probable that this silicic acid also proceeds from perfectly decomposed felspar; the presence of quartz-sand admits of the conclusion that a granite rock has been present, of which it is the *sediment*. Might not, in this instance also, sulphuretted hydrogen have been present, which, evolved in the deeper parts of the earth, has streamed into the rock above-mentioned, and has effected its decomposition?

3. It has long been known that silica displaces carbonic acid from its combinations at a red heat. But I have found that this decomposition goes on to a slight degree even at the boiling point of water. If a solution of carbonate of soda is boiled with silica, in

\* Annal. des Mines (4) T. 10, p. 69.

† In the Solfatara, near the hill of Kalamo, where an elevated temperature prevails, the superficial soil consists of a sand, in which sulphur, alum, and cimolite are ingredients. The cimolite contains some sulphuric acid, hydrochloric acid, with traces of alum and chloride of sodium. It is the latter, no doubt, which, being decomposed by means of sulphuric acid, yields the free hydrochloric acid.

‡ Compt. rend. 1846. T. 22, p. 257.



its soluble state, carbonic acid is disengaged, and the solution then contains bicarbonate of soda. If the silica which separates upon cooling is washed until it no longer has an alkaline reaction, then treated with hydrochloric acid, and the solution evaporated to dryness, chloride of sodium remains behind. The soda was therefore combined with silica and not with carbonic acid. Consequently silicate of soda exists in boiling springs which, like those of Iceland, contain soda and silica.

It is evident that the carbonic acid separated in the decomposition of carbonate of soda by silica unites with that part of the carbonate which remains undecomposed. The existence of this bicarbonate of soda is, however, only momentary, as it is continually decomposed by the heat. But when the solution cools this decomposition ceases; hence bicarbonate of soda is found in it.

A solution of carbonate of potash is acted upon by silica in precisely the same manner as a solution of carbonate of soda.

When a solution of an alkaline carbonate is boiled over silica in its insoluble modification, carbonic acid seems to be as abundantly disengaged as when soluble silica is used. Alkaline silicates therefore appear to be formed in this manner as well from insoluble as from soluble silica. I have found that when water is distilled over mixtures of carbonate of lime (artificial or granular limestone), carbonate of magnesia or spathose iron, with artificially prepared silica or powdered quartz, carbonic acid passes over with the aqueous vapour, causing a very distinct precipitate in lime water. These carbonates are therefore decomposed by silica at the boiling temperature of water. Whether the decomposition is complete when the action is long continued has not been determined.

4. It is well known that alkaline carbonates decompose solutions of sulphates of lime or magnesia, chlorides of calcium and magnesium. If, therefore, rocks contain such earthy salts, and their alkaline silicates are partially converted into carbonates by the action of carbonic acid, then double decompositions take place as soon as these salts are dissolved, earthy carbonates and alkaline sulphates or chlorides resulting. If the entire quantity of carbonic acid in the water has not been consumed in the decomposition of the alkaline silicates, the remainder dissolves, wholly or partially, the earthy carbonates formed.

Many mineral waters which contain earthy carbonates, alkaline sulphates, and chlorides, may be formed by such decompositions. If the alkaline carbonates, formed by the action of carbonic acid on alkaline silicates, are not sufficient for the total decomposition of

the earthy salts, a part of these remain dissolved in the water. These earthy salts are likewise frequently found in waters, together with earthy carbonates, alkaline sulphates, and chlorides. If, on the contrary, the alkaline carbonates are more than sufficient for the decomposition of the earthy salts, a part of those carbonates remain in the water. This is the case in carbonated springs, for owing to their large quantity of carbonic acid, the conditions exist for a considerable formation of alkaline carbonates.

5. Alkaline carbonates decompose silicate of lime.\* If a solution of carbonate of potash is poured upon this salt and the liquid filtered after some time, the residue, when washed until it no longer shows an alkaline reaction, is almost wholly dissolved by hydrochloric acid with effervescence, nearly all the silica having been replaced by carbonic acid. This interchange of acids may be recognised to a slight extent in treating wollastonite and wernerite with a boiling solution of carbonate of potash.†

Berzelius‡ analysed the interior and exterior parts of an ancient flint knife which had been altered upon the surface, and found that it contained—

			Interior.	Exterior.
Potash	...	...	1·34	3·2
Lime	...	...	5·74	3·2
Peroxide of iron and alumina			1·20	

It is obvious that the lime could only be removed in solution, and the superficial change appears, therefore, as he remarks, to have been owing to the constant action of a liquid containing minute traces of potash which gradually replaced the lime. It is, moreover, evident that the change has taken place during the historical period, for we cannot suppose that our predecessors should have made a cutting instrument of a flint partly softened by decomposition. Here, then, we have evidence of the actual displacement of lime by potash in one of the hardest and most impervious minerals, the principal constituent of which is not acted upon by water. Bearing this change in mind, we cannot be surprised at finding wernerite converted into mica, a process which consists merely in the replacement of lime by potash.

It will subsequently be shewn that such replacements are of

\* The silicate of lime used in this and subsequent experiments was prepared by decomposing chloride of calcium by silicate of potash, obtained by dissolving silica in its soluble form in boiling potash. The silicate of lime precipitated was washed until it had no longer any alkaline reaction.

† Bischof, German Ed. Vol. 2, p. 421.

‡ Jahresbericht, Jahrg. 21, p. 187.

frequent occurrence, and explain the formation of many pseudomorphous minerals.

Let us now examine more minutely the action of meteoric water upon rocks. When filtering through rocks, containing alkaline silicates, the first action will consist in the partial decomposition of these substances by the carbonic acid contained in the water, and the formation of alkaline carbonates which are dissolved. If the water thus impregnated, on penetrating further below the surface, comes in contact with calcareous silicates, another change will take place, giving rise to alkaline silicates, which replace the decomposed silicate of lime and carbonate of lime which is dissolved, if the water still contains sufficient carbonic acid. It may appear singular that the alkaline silicates should be left while the far less soluble carbonate of lime is carried away. But this difficulty is removed when we remember that alkaline silicates combine chemically with other silicates, producing double salts, which are among the most sparingly soluble minerals. We must therefore suppose that their retention is owing to their combination in the nascent state with such other silicates as may be present. Carbonate of lime, however, does not combine with silicates, and is consequently either removed in solution or likewise deposited, when free carbonic acid is absent. This view would account for the frequent occurrence of this substance, as calc-spar covering altered minerals, which still contain undecomposed silicate of lime.

Even if the rocks at different depths are uniform in composition, the chemical action resulting from the contact with meteoric water near the surface will differ from that taking place at a greater depth. In the former case simple elective affinity alone comes into play; the carbonic acid in the water abstracts portions of the bases from silicates of potash, soda, lime, protoxide of iron, &c., silica being liberated. Hence we find rocks containing silicate of lime frequently effervesce slightly when touched with acids, and this is the case even when the colour, lustre, and hardness are either not at all or but very little altered. This test gives therefore very delicate means of detecting minute incipient alterations in rocks containing silicate of lime.

The oxygen of meteoric water can only effect a partial peroxidation of the protoxides of iron and manganese present in rocks. During the initial stage of this action it is only possible to detect minute brown spots on their surfaces by means of a microscope. A brownish surface is often associated with the effervescence above mentioned. But it does not unfrequently

happen that rocks, basalt, for instance, effervescing strongly with acids, have preserved their original colour. On the other hand, basalt occurs which has become brown throughout, and still does not show any effervescence. This is, however, only observed in the last stage of decomposition, when the carbonate of lime formed by the decomposition of silicate has been dissolved out, while the greater part of the protoxide of iron was converted into peroxide, which has remained together with the silicate of alumina. In such cases the basalt is more or less disintegrated, and may be broken with ease.

On breaking columns of basalt I have frequently observed wet patches, like rain drops, upon the fractures, and sometimes quite in the centre of the mass, affording positive evidence of the permeability even of so compact a rock as basalt. If this penetration of water is continuous, the oxygen and carbonic acid of the water will gradually cause the formation of peroxide of iron and carbonate of lime. The occurrence of brown patches in broken basalt is intimately connected with this fact. The penetration of water into basalt would seem to indicate the existence in it of extremely fine fissures, and, indeed, I have sometimes detected such by the aid of the microscope, or by applying an acid round the brown patches. In the latter case effervescence was observed in a line from the patch to the surface of the basalt, indicating the position of the fissure, which was then examined with the microscope. On entering these fissures the carbonic acid of the water has converted the silicate of lime into carbonate all round. The brown colouring was only to be recognized at the inner end of the fissure, and it is therefore obvious that the formation of carbonate of lime preceded the peroxidation of the iron. It must also be observed that on touching the brown patch with acid there was an effervescence all round it.

It can scarcely be necessary to point out the falsity of the opinion held by some geologists that all the carbonate of lime in rocks, consisting chiefly of silicates, was either produced simultaneously with them, or has been deposited from water penetrating the rocks. This view is inconsistent with the fact that, with the exception of a few instances, effervescence with acids is observed only in rocks containing silicate of lime. After examining a great number of specimens of granite, I have found only one which showed even an extremely feeble effervescence. Now it is known that silicate of lime is very seldom present in granite, and only in very small quantity. Thinking, however, that a granite containing



oligoclase somewhat decomposed might perhaps effervesce, I endeavoured to meet with such a one, and, indeed, my anticipation was fulfilled. When a piece of such granite is placed in water and an acid dropped in, the escape of carbonic acid gas, from the oligoclase crystals alone, may be distinctly observed.\* Specimens of syenite, the hornblende of which was somewhat decomposed, presented the same phenomenon. Carbonic acid also escaped only from between the surfaces of the crystals and the matrix. Decomposition is always observed in rocks where large crystals are situated, because there the interstices more readily admit water.

6. Alkaline carbonates do not decompose silicate of magnesia. The artificial silicate digested for twenty-four hours, or boiled continuously, with a solution of carbonate of potash, and then carefully washed, did not effervesce the least with acids. If a mixture of steatite and solution of carbonate of soda be evaporated to dryness, and the residue washed, not a trace of magnesia can be detected in the liquid, nor does the steatite effervesce. Consequently no double carbonate of soda and magnesia is formed.

7. Alkaline carbonates decompose fluoride of calcium both at  $212^{\circ}$ , and at ordinary temperatures, carbonate of lime and alkaline fluorides being formed.†

8. Alkaline silicates decompose sulphates of lime and magnesia, and chlorides of calcium and magnesium; silicates of lime and magnesia, and alkaline sulphates or chlorides being formed. These reactions may readily be observed on the mixture of aqueous solutions of the respective salts, the sparingly soluble earthy silicates being precipitated.

The alkaline silicates being constituents of felspar and zeolites, and the most soluble of all silicates, there can be no

\* It is scarcely necessary to observe that the water should previously be boiled, so as to expel any atmospheric air which may be contained in the pores of the granite. In this way the smallest quantity of carbonic acid may be detected.

† In the German edition T. I, p. 496, I have shown that this reaction takes place at  $212^{\circ}$ . As the natural fluor spar, which is so often impure, was employed in these experiments, I repeated them with pure artificial fluoride. This, when boiled for some minutes with a solution of carbonate of soda, separated and washed until no longer alkaline, dissolved partially, with strong effervescence, on the addition of dilute hydrochloric acid, showing that the fluoride had been partially decomposed. The filtered liquid, neutralized with acetic acid, gave with lime water a precipitate of fluoride of calcium, showing the presence of fluoride of sodium. When fluoride of calcium was treated for 12 hours with a solution of carbonate of soda at the ordinary temperature, the same reaction was observed. The effervescence with dilute acid was, however, more feeble, shewing that less fluoride of calcium was decomposed than at the boiling temperature.



doubt that they are present in the waters of springs. If the above mentioned earthy salts be also present, it is obvious that silicates of lime and magnesia will be formed. We must even consider it very probable that water, in which these earthy salts are dissolved, greatly facilitates the decomposition of felspar and other minerals containing alkaline silicates.

9. Silicate of potash and chloride of sodium give rise to silicate of soda and chloride of potassium.\*

10. Silicate of soda and carbonate of oxide of zinc, dissolved in carbonated water, give rise to silicate of oxide of zinc and carbonate of soda.†

11. Bicarbonate of lime and silicate of potash give rise to carbonate of potash and carbonate of lime, silica being liberated.‡

12. Bicarbonate of lime appears to be decomposed by hydrate of magnesia, carbonates of lime and magnesia being formed. Such a decomposition occurs in the marble of Predazzo, in the Tyrol, called predazzit, by Petzholt. According to the analysis of J. Roth,§ it consists, when unaltered of 2 eqts. carbonate of lime, and 1 eqt. hydrate of magnesia, but the decomposed marble contains only  $1.86\%$  magnesia combined with carbonic acid. It is very probable that water containing bicarbonate of lime has acted upon the hydrate of magnesia, causing the formation of carbonate of lime which was deposited, and carbonate of magnesia which was carried away. Damour has likewise found that the alteration of a grey striped limestone from the same district is connected with an increase of carbonate of lime and a decrease of magnesia. The latter, carried away by water, is again deposited in fissures as carbonate of magnesia.||

13. Bicarbonate of lime and protosulphate of iron, dissolved in

\* The silicate of potash was precipitated by alcohol from a boiling solution of silica in caustic potash, and the precipitate washed with alcohol of 30%. 2.75 grains of this silicate dissolved in water was mixed with 5.5 grains chloride of sodium, also dissolved; the whole was slightly evaporated, during which some flocks separated and finally alcohol was added. The filtered liquid contained chloride of potassium, equivalent to 1.16 gr. potash. The precipitate treated with hydrochloric acid, and evaporated to dryness, gave 0.097 potash, and consisted, therefore, chiefly of silicate of soda. Although the decomposition was not complete, still the experiment is sufficient to prove that it does take place.

† Vict. Monheim in German edition, T. 2, p. 1203.

‡ This remarkable decomposition takes place when a solution of silicate of potash is added to a solution of bicarbonate of lime. The precipitate formed dissolves with effervescence in hydrochloric acid, silica being separated. It will subsequently be shewn that this decomposition actually takes place in nature.

§ Journ. für pract. Chemie. T. 52, p. 346.

|| Bullet. de la Soc. Géolog. de France. Deux. Série. T. 4. 1847, p. 1052.

water, give rise to sulphate of lime and protocarbonate of iron. The latter passes rapidly into peroxide.\*

14. Bicarbonate of lime and sulphate of copper in solution form sulphate of lime and carbonate of copper.

15. Bicarbonate of lime and sulphate of zinc form sulphate of lime and carbonate of zinc.

16. Bicarbonate of magnesia and silicate of lime form bicarbonate of lime and silicate of magnesia.† It will subsequently be shewn that magnesia frequently replaces lime. It appears in the highest degree probable that this replacement takes place in the above manner, for bicarbonate of magnesia is frequently present in water, and such water filtering through rocks, containing silicate of lime, will naturally cause this change.

17. Bicarbonate of iron and silicate of lime form protosilicate of iron and bicarbonate of lime.‡

18. Neutral or basic phosphate of lime dissolved in carbonated water, and alkaline silicates, form silicate of lime and alkaline phosphates.§

19. Phosphate of lime dissolved in carbonated water, and alkaline carbonates, form carbonate of lime, which is precipitated, and alkaline phosphates, which remain in solution.||

20. Phosphate of lime dissolved in carbonated water, and protocarbonate of iron, form protophosphate of iron, which is precipitated, and bicarbonate of lime, which remains in solution.¶

\* In the German edition, Vol. 2, p. 1201, I have noted the cautions to be observed in making this experiment.

† The sparingly soluble silicate of lime was treated with hot water, in order to obtain a saturated solution, which gives a precipitate with bicarbonate of magnesia. When cold water was employed for making the solution, no precipitate was formed until the following day.

‡ The bicarbonate of iron was prepared by passing carbonic acid through water with iron filings in a close vessel. The solution was mixed with silicate of lime in a bottle, which was closed and allowed to stand. On the third day ochre-yellow flocks had separated, consisting of persilicate of iron. The liquid filtered from this precipitate, evaporated to dryness, gave an ochre-yellow residue, which effervesced with hydrochloric acid, showing the presence of carbonate of lime. —German Ed. Vol. 2, p. 783.

§ In the subsequent experiments, neutral or basic phosphate of lime dissolved in carbonated water were always employed; the precipitates produced by the basic salt were, however, always larger, because it is more easily soluble in carbonated water than the neutral.

|| According to Lawrence Smith, on the other hand, carbonate of lime is decomposed when digested with a solution of an alkaline phosphate, phosphate of lime and carbonate of this alkali being formed. The decomposition, however, is never perfect. Chem. Gaz. No. 57, p. 100.

¶ If the carbonate of iron is prepared in the above manner, and the bottle containing the two solutions closed, to prevent oxidation, after several hours, an almost white precipitate is formed. The protophosphate of iron is, therefore, less soluble in carbonated water than phosphate of lime and protocarbonate of iron.

21. Phosphate of lime and protosulphate of iron form sulphate of lime and protophosphate of iron, the latter precipitate is pale yellow, and when persulphate of iron is used, still more yellow.

22. Phosphate of lime and sulphate of copper form sulphate of lime and bright green phosphate of copper, which is precipitated.

23. Fluoride of potassium and artificial silicate of alumina form fluoride of aluminum and silicate of potash.\*

24. Fluoride of sodium and silicate of lime form, even at the ordinary temperature, fluoride of calcium and silicate of soda.†

25. The decomposition of silicate of magnesia and fluoride of sodium proceeds very slowly, affording another proof of the permanence of this silicate.

26. Fluoride of sodium and phosphate of lime, dissolved in carbonated water, form phosphate of soda and fluoride of calcium, which is precipitated.

As alkaline carbonates are most commonly present in water, and fluor-spar occurs in many rocks, especially in dykes, it is very probable that the above reaction (No. 7) frequently takes place, alkaline fluorides being introduced into the water. But their presence can only be detected when no earthy silicates are contained in the water, for otherwise, on evaporating the water, earthy fluorides will remain. It is known that the insoluble residue obtained from the evaporation of mineral waters does sometimes contain fluorine. It would in all probability be oftener found, if Dr. Wilson's‡ new process for detecting fluorine in the presence of silica were employed, for owing to the presence of silica in these residues, fluorine can only be detected according to the method hitherto adopted, when the fluoride far exceeds in quantity the silica.

Fluor-spar is one of those minerals whose solubility in water can be easily determined. Wilson§ found that one part required 26,923 parts of pure water for solution; therefore it may be carried away not only by water containing carbonated alkalies, but also by pure water. In the former case, the carbonate of lime formed may also be removed, as it is far more soluble than the fluoride. The frequent displacement of fluor-spar by other

\* Bischof, German Edition, Vol. 1, p. 501.

† Ibid. p. 505.

‡ Read before the Royal Society of Edinburgh, and communicated to me by Professor Jameson.

§ Edinb. New Phil. Journ. Vol. 49, p. 230.

minerals, its total disappearance from many metalliferous veins in the Saxon Erzgebirge\* are sufficiently accounted for by the fact of its solubility.

27. Alkaline and earthy sulphates are reduced by carbonaceous substances in the wet way into sulphurets. This decomposition takes place in mineral waters which contain sulphates, especially sulphate of soda and organic matter, when kept for some time in corked bottles, they acquire an odour of sulphuretted hydrogen.†

The so-called fetid gypsum is a sulphate of lime which has been partially converted into sulphuret of calcium by contact with organic matter and water. Hepatite shews that even the very sparingly soluble sulphate of baryta suffers the same decomposition.

28. Alkaline and earthy sulphurets decompose protocarbonate of iron and hydrated peroxide, giving rise to sulphuret of iron.‡ If, therefore, a mineral water contains sulphates, protocarbonate of iron and organic matter, the conditions for the formation of sulphuret of iron are complete, and iron pyrites is actually formed in this way. (Chapt. IX.)

29. Water saturated with carbonic acid dissolves  $\frac{1}{4108}$  of its weight of artificial carbonate of zinc. Sulphuret of potassium precipitates from this solution white sulphuret of zinc.§ If, therefore, water contains alkaline or earthy sulphate, organic matter, and carbonate of zinc, the conditions for the formation of zinc blende are complete.

30. Sulphuret of potassium and chloride of magnesium mutually decompose each other, hydrated magnesia, sulphuretted hydrogen, and chloride of potassium being formed. The greater part of the chloride of magnesium remains undecomposed. Consequently water is decomposed in this reaction, the oxygen uniting with magnesium, and the hydrogen with the sulphur of the decomposed sulphuret. The magnesia is precipitated as hydrate, and the sul-

\* Breithaupt über die Aechtheit der Krystalle, etc. p. 40.

† This decomposition is effected not only by the organic matter dissolved in water, but also by accidental impurities, such as pieces of straw, &c.

‡ Hydrated peroxide of iron, treated with a solution of sulphuret of potassium in a closed vessel, becomes black, and, after being washed, evolves sulphuretted hydrogen on being treated with hydrochloric acid. Forchhammer found that ferruginous clay behaved in the same manner.

§ As long as this sulphuret of zinc was not entirely precipitated, it deposited readily, and the liquid passed through the filter quite clear. But when there were only a few drops of sulphuret of potassium in excess, it became milky; even after 24 hours no precipitate was deposited, and the liquid passed through the filter turbid. It became clear when boiled, and turbid again on cooling.



phuretted hydrogen unites with the undecomposed sulphuret of potassium.\*

31. The same decomposition occurs with sulphuret of barium and chloride of magnesium, hydrate of magnesia, chloride of barium, and a compound of sulphuret of barium with sulphuretted hydrogen being formed, and a part of the magnesia salt remaining undecomposed.†

32. Sulphuret of barium and chloride of calcium decompose each other; hydrate of lime, chloride of barium, and a compound of sulphuret of barium and sulphuretted hydrogen being formed, and a part of the chloride of calcium remaining undecomposed.‡

The above mentioned decompositions (Nos. 30, 31, and 32), justify the general conclusion that all alkaline and earthy sulphurets produce the same effects. Even the sparingly soluble sulphuret of calcium causes a cloudiness in a concentrated solution of chloride of magnesium. These decompositions appear, as we

\* Even when a concentrated solution of sulphuret of potassium is added to a concentrated solution of chloride of magnesium, no precipitate is formed until after some time, and when washed, decreases slightly in quantity. It was washed in a closed glass, so that no carbonic acid could be absorbed. I at first imagined that this precipitate was sulphuret of magnesium, but it proved not to be the case; for, on the addition of a solution of chloride of copper and hydrochloric acid, no gas was disengaged, and the chloride of copper was not in the least blackened. In both the following experiments, 31 and 32, the same results were observed. When a concentrated solution of sulphuret of potassium is added to a concentrated solution of chloride of magnesium until there is no longer any precipitate formed, the magnesia separated amounted to 4·64%, and, in the filtered liquid, contained 95·36%.

† On mixing concentrated solutions of sulphuret of barium and chloride of magnesium, a precipitate is immediately formed, and a very distinct cloudiness was produced on mixing very dilute solutions. When a concentrated solution of sulphuret of barium is added to a concentrated solution of chloride of magnesium, until there is no longer any precipitate formed, the magnesia precipitated amounts to 82·35%, and that in the filtered liquid to 17·64%. In this case, therefore, by far the greater part of the chloride of magnesium is decomposed. When the precipitated magnesia was dried at 212°, it lost in stronger heat some water; it was, therefore, precipitated in the form of hydrate, as it undoubtedly always is in this case. The quantity of water, however, was not determined. The circumstance that in this experiment so much chloride of magnesium is decomposed, while so little is decomposed by sulphuret of potassium, undoubtedly depends upon the formation of the double chloride of potassium and magnesium. The already-mentioned diminution of the hydrate of magnesia formed by the reaction of sulphuret of potassium and chloride of magnesium, when the precipitate was washed, is probably also owing to the same cause.

‡ On mixing concentrated solutions of sulphuret of barium and chloride of calcium, a precipitate is immediately formed, but even when very dilute solutions are used, a cloudiness is still produced. On adding a concentrated solution of sulphate of barium to a concentrated solution of chloride of calcium, until there was no longer any precipitate formed, the lime precipitated amounted to 48·73%, and that in the filtered liquid to 51·27%. As some lime would be dissolved in washing the precipitate, it may be assumed that half of the chloride of calcium is decomposed, and the other half not.



shall see in Chap. xviii., actually to take place in some brine springs.

As chloride of magnesium occurs very frequently, (it being a constituent of sea water, brine springs, and the water of several lakes, such as the Dead Sea and several salt lakes in Russia,) it is not uninteresting to have become acquainted with reactions in which this salt is decomposed. The alkaline and earthy sulphurets, the decomposing agents in this case, are certainly not uncommon; for they are formed wherever decaying organic matter acts upon alkaline and earthy sulphates, and are actually found in sulphuretted springs. The presence of compounds of these sulphurets and sulphuretted hydrogen in the water of these springs (chloride of magnesia is also present), is explicable by the preceding facts. The formation of iron pyrites and sulphuret of zinc does not admit of explanation, except by the presence of these alkaline or earthy sulphurets. It is very probable that all metallic sulphurets occurring in nature have originated in this way. The decomposition of chloride of magnesium by alkaline or earthy sulphurets cannot, therefore, be uncommon. It is probable that the certainly rare occurrence of hydrate of magnesia in nature is a result of such a decomposition, although it may be conjectured that this substance would be frequently converted by carbonic acid into carbonate (magnesite), or else into hydrated carbonate (hydromagnesite). The occurrence of magnesite mixed with carbon in the pygs of Hall, in the Tyrol, shows the possibility of such a mode of formation.

Since magnesia plays so important a part in the production of so many pseudomorphs, the acquaintance with the behaviour of this earth, under various conditions, is calculated to contribute to our knowledge of their origin. Upon the other hand, it is not less important to learn the decompositions of sulphate of baryta, for by this means our conception of the formation of this extremely sparingly soluble salt, and its displacement by other substances, is facilitated.

33. It is well known that the sulphates of lime and magnesia are decomposed by chloride of baryum.

Reviewing the foregoing series of processes of decomposition, we observe that carbonic acid, bicarbonate of lime,\* and the

\* The behaviour of bicarbonate of magnesia being so similar to that of bicarbonate of lime, there can be no doubt that in most cases the latter will act in the same way as the former. The two carbonates, as is known, occur for the most part in company in spring waters, the bicarbonate of magnesia, however, being commonly in smaller quantity than the bicarbonate of lime.

alkaline carbonates, bring about most of the decompositions and changes in the mineral kingdom. Carbonic acid and bicarbonate of lime belong to the most generally distributed ingredients, not merely of springs, but of rivers, lakes, and seas. The alkaline carbonates are not generally distributed in waters; for in those which contain sulphates of the earth, chloride of calcium, or chloride of magnesium, &c., they cannot be present. With the exception of such waters, however, they rarely fail in water. It is easy to see that it is a matter of great importance to find that the same substances which give rise to so many decompositions in the mineral kingdom, are the chief ingredients in the waters.

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## CHAPTER II.

### PSEUDOMORPHOUS MINERALS.

THE term pseudomorphous is applied to such minerals as possess geometrical forms foreign to them, and acquired in a way entirely different from crystallization.

“When it is borne in mind that the changes here alluded to do not take place in small and rarely found crystals only, but are exhibited in extensive rock formations, the importance of the subject to mineralogists and geologists will be at once apparent.”\*

Blum divides pseudomorphs into two classes, which contain respectively two and three sub-classes.†

1. Alteration-pseudomorphs ; these are produced either
  - a. by removal of constituents,
  - b. by addition of constituents, or
  - c. by exchange of constituents.
2. Displacement-pseudomorphs ; produced either
  - a. by incrustation, or
  - b. by replacement.

Thus, for example, malachite in the forms of red oxide of copper belongs to the first class, because the change has clearly consisted in the addition of oxygen, carbonic acid, and water, to the latter mineral. On the contrary, hornstone in the forms of

\* Reports of the Assoc. of American Geologists and Naturalists. Boston, 1843, p. 242.

† Die Pseudomorphosen des Mineralreiches, 1843, and Nachträge, 1847 and 1852.

calc-spar belongs to the second class, because from the absence of any chemical relation, which would explain its formation by substitution, we must conclude that the one mineral has been removed and the other introduced in its place.\*

This classification is certainly quite appropriate, and in speaking of pseudomorphs in the subsequent parts of this work, these terms will always be employed when it is desired to point out whether the change has consisted in alteration or displacement. In other cases the word pseudomorph is used in its widest sense. However, it is sometimes difficult to determine in which way the change has been effected. This is especially the case when the pseudomorph and the original mineral contain a common constituent. For instance, spathic iron occurs in the form of calc-spar, from which it might be produced by the substitution of protoxide of iron for lime. Since, however, protoxide of iron does not naturally exist, this change is impossible, and this variety of pseudomorphous spathose iron must therefore have been produced by a replacement of carbonate of iron for the carbonate of lime in calc-spar.

Such a formation of pseudomorphs by displacement must be assumed wherever the substance which would have effected the pseudomorphic change by substitution does not exist naturally.

Steatite occurs in the form of dolomite, magnesia being a common constituent; but it would be inconsistent with the laws of chemical combination to suppose that in this case the carbonic acid of the dolomite had been exchanged for silica, which does not decompose carbonates in the wet way at ordinary temperatures.

Steatite likewise occurs in the form of quartz, but we cannot suppose that the change here indicated was chemical, for neither does magnesia exist as such in water, nor does it combine with silica in its insoluble modification. Again, it would be equally inconsistent with the above-mentioned laws to suppose that carbonate of magnesia, so frequently present in water, had together with silica formed steatite. Consequently, these pseudomorphs can only have been produced by replacement.

On the contrary, it cannot be decided at all whether carbonate of lime in the forms of gypsum results from an alteration of the

\* Some geologists hold that there is a third class of pseudomorphs produced by a deposition of substances in cavities left in rocks by the solution of imbedded crystals. This process would be analogous to casting in a mould. There does not, however, appear to be any evidence in favour of this view, or any probability that a crystallizable mineral introduced into such a cavity would assume the form of the cavity, and not that proper to itself.

latter or from a replacement. The contact of water, containing carbonate of soda, with gypsum would have given rise to the formation of carbonate of lime and sulphate of soda, by substitution of the sulphuric acid in gypsum for carbonic acid. If, however, the water coming into contact with gypsum contained bicarbonate of lime, sulphate of lime would have been dissolved and carbonate deposited in its place.

In some cases replacement may be preceded by alteration, one product of which is removed while another remains with the displacing substance. When it is remembered how manifold may be the play of affinities between the constituents of a mineral and those of the water with which it is in contact, it will be evident that we are not always in a position to trace minutely the true course of pseudomorphic changes.

The fact, that among the first class of pseudomorphs we find the most complex minerals, appears to afford some clue to their origin. The reason why mica, ophite, chlorite, &c., occur as alteration, but not as displacement-pseudomorphs, is simply that they may be formed by the alteration of existing minerals at the cost of the mineral substances in water, although they cannot be formed from the latter alone. If mica could be formed directly from the substances contained in water, we might expect to find it in displacement-pseudomorphs as we do spathose iron or meerschauum.

The pseudomorphic changes commence sometimes at the surface and advance towards the interior, and sometimes in the interior. Incrustation pseudomorphs are produced by the deposition of a mineral substance upon the surface of crystals, which are for the most part entirely removed, while hollow aggregates and crystals, which are rough and drusy upon the surface, are formed. Replacement commences at an exterior point, and proceeds from thence inwards. It is seldom that remains of the original minerals are met with in these pseudomorphs at the extreme corners or the points opposite those first displaced; generally they have disappeared entirely, and their previous existence is recognizable only by the forms which remain. It may also happen that a mineral is in the first place incrustated by the action of another substance, and that it is replaced subsequently underneath this incrustation.

It is the business of the chemist to decipher, as far as may be possible, the precise nature of the processes which have given rise to the production of pseudomorphs. These processes may be



regarded as having a general analogy to the action of saline solutions upon solid bodies which are either very sparingly or not at all soluble.

Thus, the production of alteration-pseudomorphs by removal of constituents would resemble the action of alkalis upon basic sulphate of alumina. The sulphuric acid is removed by the alkali, and alumina remains. Or it resembles the decomposition of some silicates by solutions of carbonated alkalis.

The production of pseudomorphs by addition of constituents, resembles the conversion of sulphurets into sulphates: for example, iron pyrites into sulphate of iron. Oxygen is absorbed, and the meteoric water removes the sulphate formed.

The production of the other pseudomorphs of this class, those resulting from an exchange of constituents, resembles the action of a solution of carbonated alkalis upon sulphate of baryta or lime.

The production of displacement-pseudomorphs resembles the action of metallic solutions upon metals. A zinc rod, placed in a solution of lead, is gradually replaced by lead. If the solution is made to run over the rod, the zinc is removed in solution, and replaced by lead. It also resembles the action of carbonate of lime on some metallic salts, for instance, salts of iron; the carbonate disappears, and hydrated peroxide is separated.

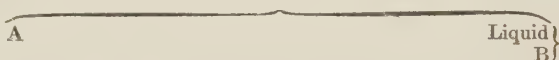
These changes are familiar to the chemist, and it cannot, therefore, appear strange to him that analagous changes should take place in nature. The only difference between the two cases is, that those effected in the laboratory occupy but a short time, and are frequently instantaneous; while those which take place in nature, result from the long-continued feeble action of minute quantities of substances dissolved in waters, still more retarded by the very sparing solubility of the substances separated from minerals in a state of pseudomorphic change. Even in our laboratories, differences in the duration of processes are recognizable, proportionate to the concentration of the solutions employed. The more concentrated they are, the more rapid are the reactions. The precipitation of lead by zinc goes on slower when the solution is dilute. Precipitates from concentrated solutions are often completely deposited in a few minutes, while those from dilute solutions remain suspended for days together.

The pseudomorphic processes may be simply expressed in chemical language, by saying that the original mineral, in whose form the pseudomorphous substance occurs, is the precipitant of the



substances contained in the water coming in contact with it. If only single constituents of these precipitants are removed entirely or partially, there result alteration-pseudomorphs by removal of constituents. If the precipitants take up new constituents from the water, there result alteration-pseudomorphs by addition of constituents. If both processes take place together, the result is the production of alteration-pseudomorphs by interchange of constituents. If the precipitants are wholly removed, and new substances deposited in their place, replacement-pseudomorphs are formed. Thus, for example, calc-spar is a precipitant for no less than twenty-eight minerals.

If we set out from the assumption that the pseudomorphic processes take place in the wet way, the production of displacement-pseudomorphs may be represented by the following general diagram:—

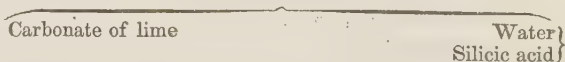


A represents the original, and B the replacing mineral. If B is dissolved in a liquid, for which A has a greater affinity than B, A is removed and B left behind. When, for example, a solution of alumina, in sulphuric acid, is dropped upon potash, the alkali unites with the sulphuric acid, and the alumina separates.



Potash here represents the original, and alumina the replacing mineral; the sulphuric acid, leaving the alumina, unites with the potash, and removes it.

The production of replacement pseudomorphs admits, in all cases, of being represented by the above general diagram. Quartz, in the form of calc-spar, will serve as an example.



A solution of silica drops upon carbonate of lime, which is dissolved by the water, and the silica deposited. Nothing is easier to conceive than this process, for carbonate of lime and silicic acid occur, in solution, in almost every fresh water. But we can also enter more into the details of this process. Let us imagine that a drop of water, containing silica in solution, falls upon calc-spar,

it dissolves the comparatively more soluble carbonate of lime, and both substances remain together in solution so long as none of the water evaporates. But as soon as evaporation commences, the sparingly soluble silica separates, and the more soluble carbonate of lime remains in solution. If the surface of the calc-spar, upon which the water falls, is somewhat inclined, the drop runs down, and thus spreads itself out, at the same time evaporating more or less. If the remainder of the drop comes to an edge of the calc-spar, it cannot drop, because the adhesion of the reduced drop to the spar is greater than its gravity. But if several drops fall, one after another, upon the same point of the inclined surface, then, after the partial evaporation, they together form a larger drop, which, from its greater gravitation, falls, and carries away the dissolved carbonate of lime.

It is evident that several conditions are necessary for the production of a replacement-pseudomorph. If the drops of water falling, as in the previous example, upon calc-spar, besides containing silica, are saturated with carbonate of lime, they cannot dissolve any of the spar; and if silica should be separated from them by evaporation, an incrustation of quartz would be formed upon the spar, without any replacement. The crystallized sandstone of Fontainebleau—a calc-spar, with an excess of quartz-sand—may have been formed in this manner. The nests, fragments, and veins of hornstone or chalcedony, in siliceous limestone, which sometimes blend very gradually with the surrounding rocky masses, may also have originated from water saturated with carbonate of lime, besides containing silicic acid; for water which has traversed limestone for some distance is, naturally, more or less charged with carbonate of lime.

The greater or less inclination of the surfaces of the minerals, the more or less rapid dropping of the water, its rate of evaporation, and certainly many other unknown circumstances, facilitate or hinder such processes. It may, therefore, readily be understood why, even in the same cavity, some crystals of a mineral may have been changed into displacement-pseudomorphs, while others have remained unaltered.

The processes concerned in the production of alteration-pseudomorphs may be represented by several diagrams. The most simple is that employed for cases of ordinary double decomposition.



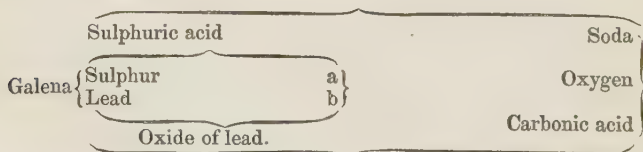
A liquid containing a substance whose constituents are C and D, falls upon a mineral whose constituents are A and B. If the sum of the affinities of A for C, and of B for D, is greater than the sum of the affinities of A for B, and of C for D, a double decomposition ensues, giving rise to the two new compounds, A C and B D. If the latter is readily soluble, and the former sparingly soluble, the same liquid which brought the compound C D, carries off B D, and A C remains behind. A B is, therefore, the original, and A C the replacing mineral.

If, for example, A B is sulphate of lime, and C D carbonate of soda, there are formed carbonate of lime, which replaces the sulphate of lime, and sulphate of soda, which is carried away by the water. We have, therefore, a process which may be represented by the above general formula.



The calc-spar previously mentioned (p. 19), in the form of gypsum, may have originated in this manner. As the gypsum contains water, and the calcareous spar is anhydrous, the water of the former was removed in this change with that which carried away the sulphate of soda.

It would not be difficult to represent the greater number of these pseudomorphic processes by such diagrams. However, as various modifications may take place according to the constituents of the solutions which cause the changes, we should, by following them out further, lose ourselves in speculation, without being able to point out the actual course of the process in individual cases. One more example may suffice to show how substances which frequently occur in waters are capable of bringing about the most opposite changes. I select the not unfrequent case of carbonate of lead in the forms of galena. Water which contains oxygen and carbonate of soda may, when continually coming into contact with galena, very easily give rise to this change, as is shown by the following diagram:—



The sulphuric acid produced by the oxidation of the sulphur

in galena is removed, in combination with soda, as a soluble salt, and carbonate of lead remains behind.

If we take into consideration the number of minerals composed of several silicates, the numerous constituents which contain water, it becomes evident how pseudomorphs may originate, in which we find only a few constituents of the original mineral.

Although, in a chemical point of view, the pseudomorphic processes present no great difficulties, still the essential circumstance of the retention of the form of the original mineral does not so readily admit of explanation. It is, however, important with regard to this point, that pseudomorphs have been produced artificially.

According to Berzelius,\* when peroxide of iron, hydrated or anhydrous, natural or artificial, and carbonate of iron, the latter either in powder or in whole crystals, are exposed to a stream of sulphuretted hydrogen at a temperature exceeding  $212^{\circ}$  Fahr., but not reaching a red heat, they are converted into iron pyrites. If crystals of these substances are operated upon, they retain their form and brilliancy, and the surfaces which were previously dull are the same in the new compounds. Even the fracture and cleavage are the same as in the original crystal: in short, these alterations present a true picture of natural pseudomorphic changes.

Cyanide of ammonium is decomposed very readily even in the atmosphere in which it has formed, yielding a nitrogenous coaly substance which retains the form of the crystals. Mitscherlich† found that when alcohol was heated over crystals of sulphate of iron, nearly to the boiling point, a decomposition ensued, although the exterior form remained unaltered. Upon taking out the crystals and breaking them, each one was found to be hollow, and presented the appearance of a geode of brilliant crystals, which were deposited upon the planes of the originals. They had the form of eight-sided prisms, and contained half as much water as the ordinary salt.

Stein‡ converted a crystal of gypsum into carbonate of lime, by leaving it for several weeks in contact with a solution of carbonate of soda at a temperature of  $122^{\circ}$  Fahr. All the streaks upon the curved surfaces of the crystal were perfectly retained, as well as the cleavage in the direction of the T-planes. He also

\* Jahresbericht, VI., p. 165.

† Poggend. Annal. T. 11, p. 179.

‡ Neues-Jahrb. für Mineral. 1845, p. 403.



succeeded in completely covering a crystal of calc-spar with hydrated oxide of iron, by placing it in a dilute solution of sulphate of iron, while the form and surfaces remained unaltered.

In these artificial pseudomorphic processes, the form of the original substance is retained only under certain conditions, the most essential being slow action,—and the same holds good in nature. If these conditions are not fulfilled, the original form is lost. The following are the most striking cases yet known, in which, at different stages of the same process of transformation, the original form has been sometimes retained and sometimes destroyed :—

Oxide of antimony in the forms of metallic antimony.

Sulphate of lead in the forms of galena.

Malachite in the form of red oxide of copper. The form appears to have been more perfectly retained in the smaller crystals, and especially when the separate crystals of red oxide were covered with a thin incrustation of psilomelane, or brown iron ore, by which their sharpness and smoothness were apparently preserved.

Purple copper in the forms of sulphuret of copper.

Kaolin in the forms of felspar and leucite.

Oxide of antimony in the forms of sulphuret of antimony.

Antimony ochre in the forms of sulphuret of antimony.

Pyromorphite in the forms of galena.

Carbonate of lead in the forms of galena.

Göthite and brown iron ore in the forms of iron pyrites.

Brown iron ore in the forms of skorodite.

Ditto ditto of cube ore.

Ditto ditto of iron spar.

Ditto ditto of specular iron.

Sulphate of iron in the forms of iron pyrites.

Cobalt bloom in the forms of smaltine.

Black oxide of copper in the forms of sulphuret of copper.

Malachite in the forms of grey copper ore.

Ditto ditto of copper pyrites.

Tile ore in the forms of grey copper.

Ophite in the forms of chondrodite. Since no positive crystalline form has been observed in chondrodite, this cannot, strictly speaking, be called a pseudomorph. But the actual conversion of this mineral into ophite cannot be doubted.

Magnetic iron ore in the forms of iron spar.

It is found that the forms of those minerals are more frequently



lost which are subject to a comparatively more rapid decomposition and alteration. It is, moreover, especially in the case of sulphurets and protoxides (protoxide of copper, protocarbonate of iron, arseniate of protoxide of iron) that the form is more frequently lost than retained.

We know that these minerals are, of all others, the most rapidly decomposed, and that this decomposition takes place with iron pyrites and especially radiated pyrites, even in mineral cabinets, in a short time. The cause of this is easily recognisable, for here they are exposed to those decomposing agents, viz., oxygen and carbonic acid, which, especially the former, have the strongest affinities. Whenever, therefore, oxygen acts energetically, as in the case of radiated pyrites, the form of the mineral is destroyed during the change, and very rarely retained.

It appears, moreover, that an incrustation formed upon a mineral, frequently preserves its form during subsequent alteration of its substance. In some cases, this incrustation consists of a substance differing both from the pseudomorphous and from the original mineral. It is also worthy of notice, that this preservation of form has frequently been effected by an incrustation of brown iron ore, as in the conversion of red oxide of copper into malachite, of galena into carbonate of lead or pyromorphite. In other cases, the coating consists of the converted substance. It is not less worthy of notice, that in the conversion of cube ore and spathose iron into brown iron ore, their forms have been preserved by an incrustation of compact brown iron ore.

This incrustation of brown iron ore, which, in the above-mentioned instances, differs from the pseudomorphous, as well as from the original mineral, affords some insight into the nature of the pseudomorphic process. It cannot be doubted, that the formation of this crust was the first step of this process; for the protecting crust must first exist before the form can be protected from destruction. Nothing, however, is more easy than to explain the formation of the brown iron ore, since there is scarcely a single instance of flowing water that does not contain, at least, traces of carbonate of iron; and no process goes on more rapidly than the transformation of this carbonate into hydrated peroxide of iron. It was, therefore, only necessary that a mineral should, from time to time, be moistened by dropping water, in order that a crust of this substance might be formed, which, like a varnish, protected the edges, corners, and surfaces of the crystal. This protection

was permanent, since the hydrated oxide of iron is one of the least changeable or soluble substances known.

Let us suppose a mineral covered with such coating, by which it is protected against external influences, especially against the action of water, in the same way that metal or wood is protected by a coating of varnish. If, however, there is only one place in which this coating of brown iron ore is not perfectly impenetrable, where, from some accidental circumstance, its formation has been prevented, the water can act here, and gradually penetrate into the interior. Thus, the whole mineral underneath the coating may be gradually changed into another, without the original form being lost.

Blum states, that an incrustation of psilomelane upon red oxide of copper has preserved its form during subsequent conversion into malachite, and that the forms of galena and grey copper have been preserved during their respective conversion into carbonate of lead and tin ore, in the one case by an incrustation of quartz, and in the other by one of compact tin ore. It is very probable that psilomelane and quartz fulfil the same office in other instances, since incrustations of these substances are by no means rare.

The hydrated oxide of iron also plays a part in the production of displacement-pseudomorphs. Thus, brown iron ore occurs in the forms of calc-spar, upon which it was evidently deposited as an incrustation, previous to the displacement of the carbonate of lime. As, however, water penetrated through one place, which was not protected by this coating, into the interior, it dissolved the carbonate of lime, and carried it away, so that then the coating alone retains the form exhibited by the original crystal of calc-spar. Quartz, in the form of heavy spar, when broken, generally presents fine streaks of peroxide of iron inside, which indicate the size of the original crystal of heavy spar, and are sections of a thin covering of peroxide of iron, which was deposited upon the original mineral. Many similar examples might be brought forward.

It still remains, with regard to the two classes of pseudomorphs, to consider whether or not the substance of which they consist is capable of assuming a crystalline form. If amorphous, there would be no great difficulty attending its deposition, in such a way as to retain the external form of the displaced mineral. But if it possesses a special crystalline form, the preservation of the form of the original mineral must be owing to peculiar circumstances. One

such is the above-mentioned incrustation, but whether or not this is the only one we must leave undecided.

Steatite, kaolin, brown iron ore, and chalcedony, in the forms of other minerals, are instances in which the substance of the pseudomorph is uncrystallizable.

The following table shows the relative frequency of these two cases among the pseudomorphs named by Blum :—

		Substance uncrystallizable.	Substance crystalline.
Alteration-pseudomorphs	...	53	61
Displacement-pseudomorphs	...	45*	34
		<hr/> 98	<hr/> 95

Among the alteration-pseudomorphs, we have quoted above (p. 26) twenty-two cases in which the pseudomorphic substance appears in its proper crystalline form, as well as in that of the original mineral. If we subtract this number from the sixty-one instances mentioned, forty-one still remain. This number comprehends, therefore, the instances in which the form of the original mineral is retained. Among these cases, however, there may be many in which under certain circumstances the original form is destroyed; for these cases are those which are most difficultly detected.

In the previous pages I have assumed that the pseudomorphic changes take place in the wet way. It is now necessary to consider more closely whether this is really the case, and whether they can reasonably be regarded in any other light.

Abundant materials for the solution of this problem have been collected by Blum. The conviction arising from the study of pseudomorphs, that their production has been extremely gradual, of itself points out to us that there are processes going on in nature which, indeed, escape our observation, but whose reality cannot be doubted. It is the fault of chemists that mineralogists have not long since arrived at the true method of accounting for these phenomena. How could they seek in waters which penetrate rocks for the cause of the changes in them, when they heard from the former that precisely those substances which play an important part, such as sulphate of baryta, silica, silicates, &c., were insoluble? Nevertheless, two sources of knowledge were

\* We have added the displacement-pseudomorphs of quartz to this class, because, in the mineral kingdom, this substance occurs more frequently in the amorphous than in the crystallized condition.

accessible to the mineralogists. That they did not avail themselves of these is not the fault of chemists.

Numerous chemical analyses have, in every case, pointed out the presence of greater or less quantities of mineral substances not only in strictly mineral waters, but also in fresh waters, and thus demonstrated their solubility, as well as the possibility that changes in rocks and minerals may take place, and new formations be produced at their cost. The mineral substances present in every crop of corn, hay, &c., the ashes left when wood is burnt, show what may be formed from the substances dissolved in water, even when there are only minute traces of them present. The large quantities of potash employed for various purposes are nothing more than products of vegetation. If plants take up from the soil, alkalies, earths, oxides of iron, silicic acid, &c., there must be some vehicle which conveys them to their roots, and this can be no other than water. Now, if these substances are thus continually transferred to vegetable organisms, why may they not be capable of producing new formations in the mineral kingdom?

Haidinger, who has prosecuted the subject of pseudomorphous minerals with such distinguished merit, considers\* that the processes by which they are formed are inexplicable by means of the known laws of chemical affinity. He has also† endeavoured to establish a classification of pseudomorphs into principal groups, upon the ground of opposite electro-chemical conditions. But I have shown‡ that there is no advantage gained by it with regard to the explanation of the pseudomorphic processes.

The fact that rain water which has penetrated rocks issues as a spring, loaded with dissolved mineral substances, is an obvious proof that this water has taken up materials from the rocks. But when water has dissolved substances, no matter in how minute quantities, it has then become a liquid capable of causing reactions, according to the laws of simple or double elective affinity.

Sulphate of baryta, one of the most sparingly soluble and least changeable bodies in the mineral kingdom, is so perceptibly decomposed by a dilute solution of a carbonated alkali, even at a temperature of from 77° to 82° F., that the change may be detected by reagents (chapter XIX). Let us suppose that water filtering

\* Poggend. Annal. Vol. 11, p. 392.

† Ueber die Pseudomorphosen und ihre anogene und katogene Bildung. Ibid. 42, p. 161 et seq., and 306 et seq.

‡ Bischof, German Edition. Vol. 2, p. 212.



through a rock has taken up carbonate of soda, and then comes in contact with baryta-spar at the above temperature, the same decomposition would take place, and if the process continued long enough, all the baryta-spar would be finally decomposed, however great might be its quantity. Here, then, is an example of a change brought about by the reaction of a substance with which the water has been charged before coming in contact with baryta-spar.

The influence of temperature upon the chemical processes in the mineral kingdom cannot be doubted; but it appears of less importance when the pseudomorphic change has taken place upon the spot where the altered minerals are found. Within the depths to which we are able to penetrate beneath the surface of the earth, and from whence we can obtain pseudomorphs, the temperatures differ so little from those upon the surface that their influence must be considered, in by far the greater number of cases, as altogether inappreciable. But when we find pseudomorphs in every stage of alteration, minerals wholly altered by the side of others as entirely unaltered, and between the two again, others partially altered, it cannot be doubted that the change is still going on.

Pressure appears to have a still less active share in the pseudomorphic process than temperature. Bunsen\* repeated the experiment of Wöhler, mentioned in Chapter III., p. 60, with a simple apparatus, in which a measurable pressure of 100 to 150 atmospheres could be produced, and found that water does not, even under a pressure equal to 79 atmospheres, exert the least action upon powdered apophyllite, and that it likewise dissolves only traces of powdered palagonite under a pressure of 103 atmospheres, while considerably greater quantities were decomposed and dissolved when these substances were boiled with water under the ordinary atmospheric pressure.† The pressure cannot, therefore, in itself have any essen-

\* *Annal. der Chemie u. Pharmacie.* Vol. 65, p. 82.

† Other experiments of Bunsen also show that pressure alone is incapable of increasing the solvent action of liquids, or, like high temperatures, of causing decomposition. Hair, which dissolves in water in a few minutes under a pressure of only a few atmospheres at a little above the boiling point, does not suffer the slightest alteration when exposed, for several hours, to a pressure of 50 or 60 atmospheres, if the temperature is not raised above 140° F. If a saturated solution of chloride of sodium, which is almost equally soluble at all temperatures between 32° and 232° F., is mixed with a small excess of solid salt and exposed to a pressure of 67 or even 100 atmospheres, there is not the slightest appearance of a further solution of the solid salt or of a separation of that which is dissolved.

Bunsen found that the carbonates of baryta of strontia, &c., dissolved in a solution of chloride of ammonium, at about 340° F., upon slow cooling, deposited prismatic crystals, frequently some millimetres in length. Here also



tial influence upon the chemical forces. James Thomson\* proved that, admitting the fundamental axiom in Carnot's theory of the motive power of heat, it follows as a strict deduction, that the melting point of ice is lowered by pressure. His brother, William Thomson,† subsequently proved that this was perceptible even under a pressure of a few atmospheres. Bunsen‡ showed that the melting point of a body may be altered several degrees by differences in pressure of scarcely 100 atmospheres. He therefore considers it as decided, that pressure has had a great influence upon the solidification of volcanic rocks, and the chemical constitution of the minerals occurring in them, perhaps even more than the conditions of cooling.

It results from these experiments, that pressure has no essential influence upon the solubility of bodies in water, nor upon their chemical affinities, although it has upon their melting points.

If there were the remotest possibility of supposing that the pseudomorphic changes could take place by igneous agency, their pressure would perhaps have some influence; but at accessible depths where pseudomorphic processes are still going on, the influence of pressure is as much excluded as that of a considerably elevated temperature.

The question as to how the play of affinities is modified in pseudomorphic processes by various circumstances, cannot be raised until a knowledge has been obtained as to the mode in which they have taken place.

There are but two modes in which we can possibly imagine these changes to have been effected—viz. by igneous or by aqueous action. Every attempt at explanation which goes beyond these limits can

there was, in the hermetically sealed tubes which were employed in these experiments, a pressure of about 15 atmospheres. If this pressure, or one twice as great, is applied to the liquid, without increase of temperature, no trace of action is perceptible. A solution of chloride of barium containing urea, heated to 275° F., consequently under a pressure of 3 atmospheres at the utmost, begins, in a few minutes, to change into chloride of ammonium, and carbonate of baryta. Exposed for six hours long to a pressure alternating between  $\frac{1}{2}$  and 30 atmospheres, not the least separation of carbonate of baryta appears.

According to these very interesting investigations, it cannot be doubted that the process patented by the brothers Siemens in Berlin, of dissolving silicic acid by digesting it in a solution of caustic potash, in a tightly closed vessel, under a pressure of 4 or 5 atmospheres, applied to the fabrication of artificial stones, depends upon the influence of the high temperature, and not upon the pressure. The caustic alkalies dissolve in this way three or four times their weight of silicic acid.—Kunst-und Gewerbbblatt, 1847, H. 15, p. 268.

\* Transact. of the Royal Soc. of Edinburgh, Vol. XVI., p. 5.

† Proceedings of the Royal Soc. of Edinburgh, Feb. 1850.

‡ Poggendorff's Annalen, Vol. 81, p. 562.

only be enveloped in language which is ambiguous, and consequently indefinite.

Let us in the first place examine the explanation given of these phenomena by those who regard them as products of igneous action, and the grounds upon which they rest their arguments.

Melted masses, very gradually cooled, crystallize when their molecules are capable of regular arrangement. Amorphous substances, like glass, assume a crystalline structure when they are heated until soft, and then cooled very slowly. The constituents arrange themselves in a different manner. Consequently, under these circumstances, there appears to be a certain mobility of the particles of substances. If the pseudomorphic change were merely a change of form, it might be supposed to have taken place in this way. However, it is a change not of form, but of the substance of a mineral, with retention of its form. Changes of substance can only take place either when constituents are separated from a compound body, when new ones are added, or when both occur together.

Such separations must therefore take place when a crystal which is formed at a high temperature, is again exposed to the influence of heat. It is true that chemistry affords examples of the decomposition of a substance at a temperature higher than that at which it was formed; for example, the oxide of mercury formed at the boiling temperature of the metal, is again decomposed by a stronger heat; but the pseudomorphic process is not of this nature.

The retention of the crystalline form implies that the subsequent heating of a mineral, formed at a high temperature, did not rise to the point of fusion. But how is it possible to imagine, that a mineral in a state of faint ignition could lose constituents and take others? How could isolated crystals in drusy cavities undergo changes by heat?

There is just as little ground for assuming that substances can be removed and introduced by sublimation; for where are they to go?—they could not be carried far by sublimation. Such assumptions with regard to minerals, such as most of the silicates whose constituents do not volatilize at the melting point, involve an impossibility, even when we do not take into account the difficulty of conceiving a cause for the re-heating of the minerals. Turn and twist the matter as we will, it is impossible to form any clear conception of a pseudomorphic process which has taken place by igneous agency.

Sublimation may take place in two ways : first, by a mechanical removal of finely divided solid bodies, as the soot is carried away by the ascending gases in a chimney ; secondly, by the transition of a substance into the gaseous state, as in the sublimation of bodies in our laboratories. Sublimations by the former process may be imagined as taking place in slightly elevated temperatures, but the assumption that they have had any geological influence is destitute of all probability. Moreover, such mechanically removed particles would scarcely arrange themselves regularly so as to form crystals, such as occur in incrustations. The second true process of sublimation would presuppose such high temperatures in the lower parts of the dykes or veins, as would suffice to convert the sublimary substance into the gaseous state. If even we assume at these depths the highest temperatures capable of volatilizing substances which appear as incrustations, like copper pyrites, fluor spar, &c., still it must not be forgotten that only the most volatile substances, like water, can retain the gaseous state at temperatures far below their boiling points. The above substances, even in the state of vapour, would condense, immediately when their temperature fell below that at which they pass into vapour. Therefore, we must suppose that the veins in which such sublimates occur with all their previously formed minerals, must have been heated throughout, to the actual focus of sublimation, to this temperature, in order to explain why the vapours were not already condensed lower down. But by what cause could such a heat have been produced, especially in sedimentary rocks ?

It is certainly true that the places where the sublimate is deposited in our artificial sublimations, gradually become heated in consequence of the condensation of the vapours, and this heating extends to the furthest point where deposition takes place. Nevertheless, if it happen that the sublimate stops up some part of the canal through which the vapours ascend, any further sublimation to more distant points naturally ceases. This would undoubtedly have happened much sooner in veins, as the small interstices between the surrounding rocky masses would soon have been stopt up. Therefore, minerals could only have been deposited in veins by sublimation very little above the place of volatilization, when the veins were not heated throughout, by some unknown cause, so that the vapours could have ascended uncondensed to the highest points. But in this case the minerals present would have been covered with the sublimate, not only on their lower side, but all round, as upon a body hung in the neck of a vessel in which sublimation is being carried on.

Thus it is evident that the sublimation-theory is incapable of explaining the alterations in metalliferous veins, and the incrustation of many minerals by others upon a particular side. If the vein fissures were previously volcanic channels, whose lateral walls had been heated by the ascent of lava, many of the minerals present might be considered as sublimates which had risen from below, in a gaseous form, subsequently to eruptions, for we actually find such sublimates in the craters of our volcanoes. However, independent of the dissimilarity of the configuration of metalliferous veins and volcanic channels, there are no traces of plutonic action on the walls of the fissures, nor any lava streams in their neighbourhood.

With regard to the fact that many substances in veins occur only on one side of previously existing minerals, it is easy to see that water, according as it enters a vein from the floor or roof of the adjacent rocks, can only run down one or other side of the minerals present, and consequently only form deposits in a particular direction. This would especially hold good when the walls of the fissures are inclined towards the perpendicular. Even if in many veins the minerals were covered with the incrustation on the under surface, this circumstance would still admit of explanation from the fact that the water drops, running down the minerals, as in the case of stalactites, first began to evaporate on the lower surface.

The following facts show the utter insufficiency of the plutonist explanation of pseudomorphic processes. Breithaupt\* mentions that incrustations of quartz, in the forms of fluor spar and calc-spar, are found in the iron mines of Schwarzenberg, Eibenstock, Johann-Georgenstadt, and especially at the Riesenberg. Upon this extensive system of red iron-ore veins there has never been a trace of calc or fluor spar found, quartz occupying the place previously filled by them. In the Saxon Erzgebirge, however, calc and fluor spar are the most frequent substances in the veins. In the cobalt and silver veins of the mine Fürstenvetrag, at Schneeberg, quartz likewise occurs in the forms of rhombohedric calc-spar and octohedral and cubical fluor spar, although at present no fluor spar is found, and the small quantity of calc-spar is never rhombohedral. It cannot be imagined how any plutonic process could have removed such considerable masses of fluor and calc-spar. Surely it will not be assumed that they had sublimed out of the veins into the atmosphere, or that they had been conveyed to unfathomable

\* Ueber die Aechtheit der Krystalle, &c., p. 40, et seq.



depths by a downward sublimation? The only satisfactory explanation of their removal, is that which assumes water to have been the agent. We do not, then, require to seek in the immediate neighbourhood for the substances removed; for whatever has dissolved in the water which has percolated through rocks, may not be deposited until it reaches the sea.

Here, as everywhere, with regard to pseudomorphic changes, the assumption of aqueous agency alone leads to a simple and satisfactory explanation. Water, together with the substances it contains, such as carbonic acid and oxygen, are the only ones which show changes of place; it is these which penetrate, according to hydrostatic and capillary laws, wherever matter is not hermetically enclosed. The fact that all earths and salts are to some extent soluble, proves the possibility of their removal and introduction.

I shall, however, bring forward still more facts which are in favour of the opinion that pseudomorphs are effected by water. W. Phillips\* mentions hollow cubes (probably derived from previously existing fluor spar), consisting of small crystals of quartz, and nearly filled with water. Freiesleben† mentions quartz in the form of rhombic calc-spar, which sometimes occurs as a thin drusy crust distinctly containing water and air. Such pseudomorphs clearly point out the mode in which they have originated.

Among the 90 alteration-pseudomorphs which Blum describes, there are not less than 59 which contain water, while the original minerals from which they are derived are anhydrous. It is scarcely possible that any one will doubt that water must have been present during these changes. Perhaps, however, in order to save the plutonic views, recourse will be had to the supposition that they were produced by the action of red-hot aqueous vapours.

The progressive conversion of felspar into kaolin, proceeding from the exterior to the interior, is caused by penetrating water. Cordierite, andalusite, wernerite, and tourmaline are anhydrous minerals, but in some varieties there is a greater or less quantity of water, which indicates the incipient alteration. Haidinger‡ remarks that the metamorphosis of cordierite commences with the absorption of water, which again decreases as the decomposition advances.

Moreover, among these 90 pseudomorphs there are 9 which

\* Mineralogy, 1823, p. 7.

† Magazin für die Oryktognosie von Sachsen, Heft. II., p. 107.

‡ Ueber den Corderite. Abhandlungen der K. Böhm. Gesellschaft der Wiss. V. Folge. Bd. 4, Prag. 1845, p. 8 et seq.



originate from the alteration of hydrated minerals. In the production of these, indeed, it does not appear necessary that water should have been present, inasmuch as the proportion of water has not increased; but it cannot be imagined that one hydrated mineral was converted into another hydrated mineral by igneous agency.

The preponderating number of hydrated substances among alteration-pseudomorphs clearly shows that water played an important part in their production. Among the remaining 22 there are 7 which, though derived from hydrated minerals, are anhydrous, and 15 in which the original and the pseudomorphous minerals are anhydrous. But this could scarcely be considered as an evidence that the changes have been effected by igneous agency; for when a mineral can only exist in the anhydrous state it will not, in crystallizing from water, take up any, as is shown by the great number of anhydrous salts which are prepared in this way.

It would be superfluous to classify in the same manner the displacement-pseudomorphs mentioned by Blum. In reference to these, where the original mineral entirely disappears and is replaced by another, there is not the remotest possibility of admitting any other explanation of the introduction and removal, than the action of water. When we find quartz in forms of heavy-spar, or brown iron ore in forms of quartz, neither the heavy-spar nor the quartz can have been removed in a state of fusion or of vapour, for they are among those substances which are fused or sublimed with the greatest difficulty, nor can the brown iron ore, which is so readily decomposed at a moderate heat, have been introduced in either of these states.

It is impossible to lay too much stress upon the fact that the pseudomorphic change commences with the absorption of water. In those cases where there are neither oxides capable of further oxidation, nor bases capable of uniting with carbonic acid, it is the action of water which tends to destroy the individuality of minerals. The absorption of water is analogous to the formation of hydrates from oxides and salts, when exposed to water or even to a moist atmosphere. Examples of this change are afforded by the alkalis and alkaline earths, anhydrous phosphoric acid when exposed to the air, the conversion of anhydrous sulphate of lime into hydrated, as in the fabrication of gypsum figures. The deliquescence of various chemical preparations, as chloride of calcium, also belongs to this class of phenomena.

Chemistry affords many examples of the more ready combination of many substances when hydrated. Alumina, peroxide of

iron, oxide of copper, &c., are dissolved more readily in acids when in the state of hydrates than when anhydrous; indeed, many are entirely insoluble in acids when in the latter state. Now, if the affinities are stronger in artificially prepared substances when they are hydrated than when they are anhydrous, it may be inferred that minerals also are more susceptible of alteration and decomposition when in the hydrated state. It is, indeed, possible that cordierite is not capable of passing through a series of changes until it has previously taken up water.

As there are artificial salts which give off their water of crystallization when exposed to the air, so the mineral kingdom presents similar phenomena. Laumontite and other zeolites effloresce in the air, giving off their water of crystallization. It is on this account that such minerals could only have been formed in spaces saturated with aqueous vapour, such as drusy cavities may be supposed to be. There are, indeed, grounds for the conjecture that many hydrates very gradually lose their water even at ordinary temperatures, like the hydrated peroxide of iron in its conversion into peroxide. Perhaps, also, andalusite and chialtolite have originated from hydrated silicate of alumina by the loss of its water.

The progressive alteration of some minerals from the interior outwards, are very remarkable phenomena, which cannot be ascribed at all to plutonic, and with difficulty to aqueous agency. In the porphyry of Teufelsgrund, in the Schwarzwald, crystals of felspar, frequently an inch in length, are found converted in the interior to a kaolin-like substance, but perfectly unaltered on the exterior. They are so fixed in the rock, that none of the outer planes are exposed. If such crystals are broken, the kaolin mass appears to be surrounded by a brilliant frame of unaltered felspar about  $\frac{1}{2}$  line broad. It is very remarkable that the water which has caused this decomposition, has penetrated into the interior of the felspar crystals, and not between them and the surrounding mass in which they are embedded, where capillary spaces might most naturally be expected; and this is the more remarkable, as the tolerably uniform breadth of the unaltered felspar shows that the decomposition commenced exactly in the centre of the crystal, and advanced regularly from thence towards the exterior. Even if it can be imagined that capillary fissures or cleavage planes extend into the interior of the crystal, it is still by no means easy to perceive why they should join precisely at the centre of the crystal, or, perhaps, several of them intersect at that point. It is

quite as difficult to understand why the decomposition has not in any single instance advanced beyond the frame of felspar. In fact, the more the details of this phenomenon are examined, the greater are the difficulties which surround it.

The microscopic bubbles of carbonic acid, evolved when acids are poured upon rocks in whose substance carbonate of lime has been formed by spontaneous decomposition, show how minute are their capillary interstices. Water can penetrate into their interior in the same way that the acid does when disengaging the carbonic acid. It is, therefore, easily conceivable that the decomposition of a crystal may commence from the interior and advance outwards, as a consequence of the action of water penetrating it in this way. But at the same time, the regularity of this phenomenon (which Blum assures me he has recognised in at least sixty specimens) remains unexplained.

Blum's descriptions of the individual pseudomorphs do not unfrequently present similar phenomena, which, like that above-mentioned, can with difficulty be ascribed to aqueous action, and not at all to that of heat. One among others of this kind, is the quartz in the form of heavy spar.\* Here sulphate of baryta must have been removed, and the replacing quartz introduced through thin layers of specular iron ore.

While it is in all cases difficult to understand how constituents or the entire substance of a compact mineral can be removed from its interior, still when the pseudomorphs present a porous structure, this appears less strange. As the process commences in the exterior of the mineral, pores are formed which facilitate the penetration of water and the further excavation of the interior parts. If, during the metamorphosis, the specific gravity of the mineral is increased, as in the conversion of hydrated peroxide of iron into anhydrous peroxide, this also tends to give the mineral a porous structure. If it is remembered that by far the greater number of pseudomorphs are porous, the gradual penetration of water into the interior may be easily understood. The diminution of the mass of a mineral, or the increase of its specific gravity, is then the cause of the penetration of water into the interior, and this penetration in its turn facilitates the advance of that alteration inwards.

The twenty-eight minerals which occur in forms of carbonate of lime, are all less soluble than it is; the less soluble mineral displaces, therefore, the more soluble. So far as it is

\* Die Pseudomorphosen, p. 224.

possible in the case of substances of very slight solubility to estimate which are more or less so, it appears that the displacing mineral is always less soluble than that which is displaced.

The deliquescent salts—carbonate of potash, chlorides of calcium, and magnesium, &c.—are the most soluble, and have a greater affinity for water than any others, condensing as they do the aqueous vapour of the atmosphere and dissolving in it. It may, therefore, be assumed with regard to minerals, that the more soluble they are the greater is their affinity for water. Consequently a mineral which never appears in the form of another, would have a greater affinity for water than those minerals which occur in its form.

The greater solubility of the displaced, in comparison with the replacing mineral, will cause the porosity of the former to increase during the pseudomorphic change. For example, if water, containing protocarbonate of iron in solution, come in contact with calc-spar, the quantity of carbonate of lime removed would be greater than the quantity of carbonate of iron supplying its place if both solutions were saturated, and consequently hollow or porous crystals must be formed, without taking into consideration that this must also result from the specific gravity of iron-spar being greater than that of calc-spar. If, however, either the introduced or the removed solution is not saturated, or if both are at different degrees from their points of saturation, the most varied modifications may result, which it is evident can only be characterized generally, and not recognised in individual instances.

According to Blum,\* the following substances are met with in petrified organic remains:—carbonate of lime, sulphates of baryta, strontia, and lime, fluoride of calcium, quartz, ferruginous quartz, opal, talc, peroxide of iron, anhydrous and hydrated carbonates of iron, zinc, and lead, black oxide of manganese, phosphate of iron, iron and copper pyrites, sulphurets of lead, zinc, copper, and mercury, purple copper, native copper, chlorite.

Nearly all these substances are also met with as pseudomorphs, chiefly of displacement, and sometimes they have constituted the original mineral in whose form the pseudomorph occurs. The occurrence of petrifications in sedimentary formations, excludes the possibility of regarding the introduction of mineral substances as in any degree a consequence of plutonic agency. It can only be ascribed to the agency of water.

We here find additional evidence in favour of the conclusion

\* Erfter Nachtrag zu den Pseudomorphosen, p. 152 et seq; Zweiter Nachtrag, p. 125, et seq.



that the pseudomorphic, as well as the petrifactive changes, have been effected in the wet way. If these substances could replace by this means the substance of organic remains, they could likewise replace or alter, by the same means, the substance of those minerals in whose form they are found.

It is impossible for the supporters of the plutonic theory to bring forward any evidence which so strongly favours their views, as the phenomena of petrification do the theory of aqueous agency.

Even the comparative insolubility of most of the substances which play a part in pseudomorphic processes, as, for example, sulphate of baryta, and more especially the metallic sulphurets, can no longer be admitted as a counter-argument, when we see in some belemnites, not only the whole sheath, but also the alveole, filled by the former, and wood impregnated throughout with it, and galena occurring in the interior of bivalves, &c. With such striking proofs of the solubility of these substances, it is no longer necessary to appeal to chemical authorities; however, it must be remembered that metallic sulphurets, and perhaps also sulphate of baryta, have not been introduced as such into the petrified organisms, but have been produced in the latter from other combinations.

If we go somewhat into the minutiae of the pseudomorphic and petrifactive processes, we meet with many analogies between them. Silica occurs as a petrifying material, in its different conditions of crystalline or common quartz, or as chalcedony, flint, hornstone, more rarely as jasper and agate. The amorphous varieties of quartz are, nevertheless, more frequent than the crystalline. We meet here with the same modification of silicic acid as in the pseudomorphs. We also find similarities to the siliceous formations in the cavities of amygdaloids. Crystalline and amorphous quartz are associated in the petrifications as well as in amethyst druses, the former occupying the interior, the latter the exterior part of the shell of molluscs.

In many belemnites, quartz and heavy spar are associated together as petrifying materials, so that the upper part of the sheath consists of quartz, and the lower part of sulphate of baryta. In many places it seems as if the latter had been displaced by silica, as in the quartz-pseudomorphs in the form of heavy spar.

The silicification of wood positively proves that it was no other liquid than ordinary water which caused it. How could the structure of wood, its annual rings, cells, and vessels, have been preserved, if the silicic acid had penetrated with violence? How could this substance have filled the open interstices of the woody



fibre, if the solution had been less fluid than all waters which contain more or less, though always a mere trace of silicic acid?

It is an interesting fact, that talc has been found as a petrifying material in a fine lamellar as well as a flaky form, white and brilliant, in vegetable remains in the slates of Petit-cœur, near Moutiers, in Piedmont; for this shows the presence of a silicate of magnesia in water, and affords some clue to the very frequent conversion of such different minerals into steatite, &c.

With regard to iron pyrites, the most frequent of all the petrifying materials of organic remains, we shall have occasion to speak in Chapter XV.

The specular iron is a very remarkable petrifying material. Blum describes a bivalve from a ferruginous oolitic rock at Thoste, near Semur (Depart. Côté d'Or), the shells of which consist entirely of an aggregate of crystalline laminæ of specular iron. A cardinia from the lower lias (Dep. Yonne), communicated to me by Beyrich, likewise consists of specular iron. Fibrous red iron ore was met with by G. Sandberger,\* as a petrifying substance, at a mine in the neighbourhood of Oberscheld in Nassau. These petrifications are of no little importance in a geological point of view, for they furnish, altogether, decisive evidence that specular and fibrous red iron ores are formed in the wet way, whether the oxide of iron occurs in veins or as a pseudomorph.

The compact brown-iron-ore does not appear to occur as an original petrifying material of animal remains, but very often as a product of altered iron pyrites. On the contrary, it is more frequently met with as the direct petrifying material of wood, leaves, and fruits. However, the *Gryphaea convexa* (Say) is not uncommonly found petrified by ochrey brown-iron-ore in the ferruginous sand of the chalk formation at Woodstown, in New Jersey.

As the brown-iron-ore occurs so frequently in displacement-pseudomorphs, and the material for its formation can only be furnished by the soluble bicarbonate of iron, it is remarkable that such waters, though frequently so occurring, have not oftener caused the

\* Jahrbuch für Mineralogie, 1845, p. 176.

This petrification is in the Edinburgh Museum of Natural History. Professor Jameson commissioned Dr. Krantz, of Bonn, to collect the most important minerals, pseudomorphs, &c., which are mentioned in the German edition of this work. I have closely examined this collection, which consists of 664 specimens, and have found many which illustrate the phenomena, described much more clearly than the minerals which I used. I shall, therefore, frequently take occasion to refer to especially characteristic specimens in this collection. Krantz is continually occupied in the collection of new and important pseudomorphs, which may always be procured from him.

petrification of animal remains. However, according to Zippe,\* spathose iron occurs as a petrifying material of wood, at the Postelberg, in Bohemia. Wisert† recently met with black oxide of manganese as the petrifying material of an ammonite, from the mines at the Gonzen, near Sargans, in Switzerland.

Brown sulphuret of zinc is frequently met with in the chambers of various ammonites of the lias limestone. With regard to the formation of sulphuret of zinc we shall have occasion to speak in Chapter IX.

Galena likewise occurs, though very seldom, as a petrifying material of organic remains. Sometimes granules of copper pyrites are found in it. Blum describes wood of Lemberg petrified by this mineral, which latter is converted, on the outside, into carbonate of lead. It is obvious that the same process has taken place here as in the veins where copper pyrites is also frequently found associated with galena.

Copper pyrites very frequently appears as a coating upon remains of fish in the cupreous slate of Mansfeld and Eisleben, and of Riechelsdorf, in Hesse. It covers the impressions of the bones, fins, and scales, but rarely replaces their substance; in which case, however, it forms an aggregate of fine granules, of their entire thickness. Vegetable remains are also found in the cupreous slate of these districts, which are petrified or incrustated by copper pyrites. Purple copper occurs in a similar manner upon the remains of fish, in the same cupreous slate of Eisleben, but more rarely than the ordinary pyrites. Sulphuret of copper is likewise found as a petrifying material of vegetable remains, in the magnesian limestone formation near Frankenberg, in Hesse. The larger remains of wood are mostly situated in alternating layers of sulphuret of copper and carbonaceous matter. In some places small and extremely thin laminæ of metallic silver are intermixed with, and sometimes cover them. In some pieces of wood, the petrifying material is converted into very beautiful fibrous malachite.

Thus, then, we find exactly those metallic sulphurets as petrifying materials, which are the most frequent in deposits of metallic ores. Although extending the idea of solubility to those substances which have hitherto been characterised by chemists as insoluble, still we must limit this extension as regards the electro-positive sulphurets above mentioned. This is the more easy, since, as I shall subsequently have occasion to show, the examples of iron pyrites

\* Jahrb. f. Mineral., 1843, p. 616.

† Ibid., 1851, p. 572.

and zincblende prove that insoluble metallic sulphurets may be produced from soluble salts of protoxide of iron and zinc. Reasoning analogically, it may be inferred that sulphurets of lead and copper have originated in such a way from soluble salts of these metals. With regard to such a formation of galena, it is to be remarked that, according to Freyer,\* in an old gallery of a lead mine specimens of charcoal were found, which were covered with crystals of galena. Blöde† describes the frequent occurrence of encrinites, converted into carbonate of lead, in veins of lead ore of the transition limestone, at Javorzno, near Kielce. Carbonate of lead is, like all earthy and metallic carbonates, somewhat soluble in carbonated water. We may, therefore, imagine that carbonate of lead is convertible into sulphuret in the same way that carbonate of iron is converted into sulphuret. Carbonate of copper has been found in solution in mine-waters, and a similar formation of sulphuret of copper may likewise be assumed.

With the exception of cinnabar, which occurs as an incrustation, though very seldom as the actual petrifying material of fossil fish, in a bituminous marl slate of the coal formation, at Münsterappel, in the Rheinpfalz, no other metallic sulphurets than those mentioned have been met with as petrifying materials.

I shall, in conclusion, notice the previously mentioned occurrence of metallic silver mixed with sulphuret of copper and organic remains. There cannot be the least doubt that this metal must have been reduced upon the spot. It also points out that the petrifying material found in organic remains has not always been deposited as such from water, but may not unfrequently have been formed from other substances, by various processes taking place upon the spot. Sulphuret of silver is one of the most easily reducible sulphurets: it is reduced by mere aqueous vapour, and although this reducing agent cannot well be admitted in this case, it is still allowable to infer that similar ones have caused the reduction.

Metallic copper also occurs, as a thin coating, upon remains of fish in the cupreous slate formation of Riechelsdorf. This is still more remarkable than the occurrence of metallic silver. Oxide of copper is, indeed, readily reduceable, but requires a high temperature, which in this case it would be inappropriate to assume. But however this copper may have been reduced to the metallic

\* Bericht über die Mittheilungen von Freunden der Naturwissenschaften in Wien von Haidinger, T. 5, p. 84.

† Jahrbuch für Mineralogie, &c., 1834, p. 638.

state, its presence upon organic remains proves the possible reduction of that widely distributed metal occurring in veins, and sometimes even in drusy cavities, by similar processes, without any interference of igneous agency.

Pseudomorphic processes must go on most extensively where the greatest quantity of water circulates, and consequently in the coarse-grained rocks. The localities in which pseudomorphs are found confirm this. Thus, the Heidelberg pinite is met with in coarse-grained granite in a dyke, the finest specimens associated with quartz in the adjacent granite.

As the veins are the storehouses of metallic ores, the greatest number of pseudomorphs consisting of the metallic compounds occur in them. Further, veins are seldom filled by a compact mass, but have numerous drusy cavities or hollows, which sometimes communicate for a considerable distance, and are on that account easily penetrated by water. The projecting crystals are most subject to these changes.

In those cases where oxygen, water, and carbonic acid cause alterations of the substances contained in veins, the pseudomorphs are principally found near the outcrop, and they often disappear below a certain depth, which is, however, sometimes very considerable, as in the mines at Holzappel, in Nassau, where carbonate of lead has been found 210 feet under the surface. These products indicate the depths to which water penetrates. In veins whose outcrops are covered by thick strata of clay, iron-spar is not converted into brown iron ore,\* because in this case water cannot penetrate to the veins.

The changes taking place in the interior of rocks, of which Blum mentions six instances, are of especial geological significance. May not the displacing substances, as in this case, have assumed the form of those which are displaced, also occur in their own crystalline form? If this does not admit of doubt, we can conceive how new minerals may have been produced from previously existing amorphous masses in the interior of rocks.

Strictly speaking, we do not know with regard to any single mineral, whether it is still in its original condition, or has been more or less altered; for they could only have preserved their original condition when entirely shut out from water and atmospheric air. But there is not a rock in which minerals are so imbedded that these two causes of alteration cannot penetrate to them to some extent.

\* Schmidt Beiträge zu der Lehre von den Gängen Siegen, 1827, p. 58.



The alteration of a mineral is an extremely slow process. The material changes, without doubt, go on so gradually that they are not chemically recognisable until after long periods of time. In the analysis of a mineral in which such changes have already commenced, especially by the addition of new constituents, although in very minute quantities, it is not unlikely to happen that they may be considered as accidental in calculating the chemical formula, and deducted, whether correctly or not is a matter of opinion. These new constituents, introduced in the course of time, are certainly foreign to the mineral in its original condition, and are on that account to be deducted. Since, however, alterations seldom take place merely by addition, but more frequently by loss of constituents, it is likewise requisite that, in the latter case, the quantities lost should be added to the analytical results. It is true, however, that this is seldom possible, and only when a mineral, in which minute quantities of foreign substances are found, has been previously analysed in its unaltered state.

I will take a simple case as an example. There are sufficient grounds for considering andalusite to be a pure silicate of alumina, although all previous analyses have pointed out, besides these two essential constituents, potash, lime, magnesia, oxides of iron and manganese, and water. Assuming that these are accidental substances, the andalusite which contains the smallest quantities of them would come nearest to the original condition. This is the case with the andalusite of Lisenz, in the Tyrol, and of Lancaster, according to the analyses of Bunsen and A. Erdmann.

Andalusite is converted into mica, in which change a part of the alumina is removed; potash, magnesia, and peroxide of iron being introduced in its place. One of these bases is always found in andalusite, sometimes several of them together; and it may therefore be inferred that this mineral, as usually met with, is already in a state of incipient alteration. The original and chemically perfect andalusite is, therefore, unknown. Thus, in order to render the analytical results complete, while these bases are deducted as adventitious, and not belonging to the compound, the alumina which has already been removed must likewise be added. But since the original quantity is, strictly speaking, unknown, the value to be added remains uncertain. Judging, however, from the quantity of the bases introduced, it cannot amount to much, perhaps little more than 1% of the mineral. Here the laws of definite proportions may be of assistance. That formula, for instance, which gave a quantity of alumina not less than what has been pre-



viously found by analysis, would be the most probable. This is the case with the formula, according to which andalusite is a compound of 3 equivalents of silicic acid and 4 equivalents of alumina.

If a mineral were found having the crystalline form of andalusite, but containing a larger quantity of alumina; or, in other words, if an inverse process of alteration had taken place, an addition of alumina, then the inference that the most probable formula is the one which gives a quantity of alumina not less than that found by analysis, would not be warranted. No other alteration of andalusite is known besides that into mica, except that into steatite. The latter change presupposes not only a partial, but a complete disappearance of the alumina, and its replacement by magnesia.

These examples will suffice to show the importance of the minute quantities of substances present in minerals, and generally considered as accidental. These substances, which are troublesome to the chemist, because he cannot introduce them into the chemical formula, acquire significance when compared with the constituents of the pseudomorphs resulting from the alteration of the mineral in question. They then no longer appear as accidental, but indicate the transition of one mineral into others, and lay before us clearly the genetic part of the conversion processes. It is on this account desirable that, in the analysis of minerals, the same attention should be paid to such apparently unessential constituents as to those which are essential. The former will, as the alteration advances, finally become essential. The minute quantities of iron and manganese in the andalusite of Lisenz, will cease to be unessential constituents when the conversion into mica has been completed; and inversely, the last remains of alumina which may be found in steatite resulting from the alteration of andalusite, are undoubtedly to be included among the unessential constituents, although this earth was essential to the original mineral.

It cannot be denied that chemical analyses of minerals acquire a much higher value when their object is not merely the establishment of chemical formulæ, but also the elucidation of their genetic origin. Mineralogists have established the important fact, that one mineral may appear in the form of another, and it is the business of chemists to point out by what processes alterations or displacement may be effected. It is but rarely that the chemist is able to produce artificially the changes observed in nature, and in order to trace the various stages of these natural processes, there remains no other course for him to pursue than to ascertain by analysis the

increase of the non-essential, and the decrease of the essential constituents, and from the nature of the former to draw conclusions as to the processes which were going on in the mineral when found.

The pseudomorphic process may be imagined to consist either in direct conversion of minute particles of the original mineral into the new substance, or in a series of intermediate stages, the results of which are minerals successively more distinct from the original in composition, and nearer to the final product. In the former case a particle of andalusite would be directly converted into mica.

From the nature of the process of displacement-pseudomorphism, only the first change can take place. In the displacement of heavy-spar by quartz, a particle of silica replaces each particle of sulphate of baryta which is removed ; here there is no intermediate stage. In the conversion of one compound, which can be prepared artificially, into another, there is as little occasion to assume any gradual transition when no intermediate compound is known. Magnetic iron ore, which is convertible into peroxide of iron, certainly does not pass through any intermediate stage of oxidation, but each particle of magnetic oxide is directly changed into peroxide.

Such direct changes, however, do not always take place. Thus, perhaps, the conversion of iron pyrites into sulphate of iron is not direct, but the sulphur more probably passes through its various stages of oxidation before reaching the highest.

It is possible that several changes may frequently have taken place before the last product was formed. Thus it is probable that carbonate of lead, in the forms of galena, resulted not from a direct alteration of the latter, but from that of sulphate of lead previously formed from galena by oxidation.

In the alterations of complex minerals, especially silicates containing several bases, there are certainly transitions in most cases, and sometimes a long series. Thus cordierite is the starting-point of a whole series of alterations, finally ending with mica ; while fahlunite, chlorophyllite, bonsdorffite, esmarkite, (perhaps also oolite), weissite, praseolite, gigantolite, and pinite, are remains of cordierite in pseudomorphic conditions.

Inasmuch as the minerals between cordierite and mica are only transition products, they cannot be regarded as individual species. The same mineral in such a transition series would vary in its composition more or less according as its alteration was more or less advanced. The chemical formulæ of such changeable substances are in themselves of little value, and especially so when it

is attempted to make use of them to explain the mode of alteration.

The statement of the per-centages of the substances found by analysis, gives the best representation of such processes, because no constituent is then omitted, however small its quantity. It is, however, but seldom that the absolute increase and decrease of the constituents can be recognised even in this way.

When it can be shown, that during the alteration, any one constituent has neither decreased nor increased, the representation becomes comprehensive and complete, if the constituent is taken as a constant quantity in the composition of the original and altered minerals. But this can seldom be proved with certainty; in general it is necessary to rest upon probabilities.\*

As petrifications are important, and in many cases indispensable aids in recognising the sedimentary *formations*, so likewise pseudomorphs are important, and frequently the only means of tracing the processes of alteration and displacement which have taken place and are still going on in the mineral kingdom. If pseudomorphs are considered merely as a means of attaining this end, it is as little necessary for us to trouble ourselves with the conditions of their formations, as it is in the determination of sedimentary formations by means of petrifications, to know in what manner they have been produced. However, in a chemical treatment of geological phenomena, we cannot consider pseudomorphs merely as existing facts; we must also investigate the processes themselves by which they have been produced. Therefore, we have in the preceding pages traced their formation as far as the present state of science permits.

Pseudomorphs furnish us with a kind of knowledge which we have no opportunity of deriving from any other source. It will scarcely ever be possible to convert augite, olivine, or hornblende, &c., into serpentine in our laboratories. But when we find serpentine in the forms of these minerals, this fact is a sufficient evidence that such a conversion can take place; and if in any given instance there are geognostic reasons for the opinion that one or other of these minerals, or even several together, have furnished the materials for the formation of serpentine, there is a high degree of probability that such a change has actually taken place.

\* In the German ed., t. II., p. 266 fol., I have constructed formulæ, in order to find whether, in some cases, during the pseudomorphic process, an increase or decrease of the constituents, or both together, have taken place.

The production of pseudomorphs appears to depend upon an incrustation of the original crystal (p. 27), or some other accidental circumstance. The number of instances in which the form of the original mineral is destroyed, and the product of the change appears in its own crystalline form, is by no means unimportant; and it would be still more important, if after completion of the change those characteristics were not wanting which might enable us to decide whether this or that mineral had furnished the material. It cannot, therefore, be conjectured that the possible conversion of one mineral into another stands in any necessary relation to the preservation of the crystalline form. When, for example, we find serpentine not in the form of augite, olivine, or hornblende, &c., but in amorphous masses, we are not, on that account, warranted in concluding that it is not a product of the alteration of those minerals; for this may have taken place under circumstances unfavourable to the preservation of the crystalline form.

If a crystalline mineral can, under certain conditions, be converted into another, whether with or without retention of form, then the same mineral in an amorphous state would certainly suffer the same change when placed in the same circumstances. Chemistry, at least, affords us no instance of a substance behaving differently in a crystalline or amorphous state. It is indifferent whether we decompose calc-spar or chemically precipitated carbonate of lime with sulphuric acid; sulphate of lime, in a crystalline state, is always formed.

We must, therefore, infer that augite or olivine, &c., placed in the necessary circumstances, may be converted into serpentine, whether they are in a crystalline or amorphous state, or in fine powder. Since serpentine has no individual crystalline form, it can evidently only appear amorphous when the material from which it has been formed was amorphous.

On the other hand, a mineral which occurs only in a crystalline state, would assume its individual form when produced by the alteration of an amorphous mass. Cordierite, tourmaline, &c., in powder, would therefore, under the necessary conditions, be converted into mica, possessing its own crystalline form, since they are subject to this change when in a crystalline state. Moreover, it cannot be doubted, that in the conversion of a crystal of cordierite into mica, the original form may, under certain conditions, be destroyed, and the latter mineral present itself in its own form.

We have already seen (p. 25) that crystallized iron ores may



be artificially converted into iron pyrites without losing their crystalline form. Wöhler\* found that an intimate mixture of calcined brown iron ore, sulphur, and chloride of ammonium, very slowly heated to a temperature just sufficient to drive off the excess of chloride of ammonium, yielded small, brilliant octohedrons, and cubes of iron pyrites. This therefore proves, that both crystalline and amorphous substances may be altered artificially, and that while in the former case the products are pseudomorphous, in the latter they assume the forms proper to themselves.

The importance of the pseudomorphic processes, and the error of those who regard them as having but little connection with the changes of rocks, is sufficiently shown by the total disappearance of previously existing substances in veins (above mentioned, p. 35). I consider that the entire removal of fluor and calc-spar from a whole series of veins, and the introduction of an equal quantity of quartz in their place, is a matter of vast importance. And how do we know that this has actually taken place? Because we find quartz in the form of fluor and calc-spar. Is it not to be inferred from this fact that far more stupendous displacements may have taken place where the processes have continued longer? To what enormous spaces of time we come, when we reflect upon the periods during which the fluor and calc-spar were introduced into these fissures, and then the periods during which these minerals were again removed by water, and quartz substituted in their place! And yet this happened after the formation of the rocks in which these fissures occur. If we imagine similar processes to have taken place in the rocks themselves, and extending over not only both those periods, but the entire space of time since their formation, we shall be compelled to admit that inconceivably stupendous changes have taken place. During the time in which a single crystal of fluor-spar is displaced by quartz, millions of similar crystals lying near it may suffer the same change if they are placed in the same circumstances.

If such phenomena as those which Breithaupt mentions are attentively considered, it cannot in the slightest degree be doubted that they recur at innumerable points; if it is satisfactorily ascertained that they are caused solely and alone by the action of water, it is not surprising that in the alterations which large masses of rock have undergone, we should again meet with results of similar processes. After such considerations, the conversion of

\* Poggendorff's Annal., t. 37, p. 238.

extensive masses of rock into steatite, talc, serpentine, kaolin, &c., cannot appear in the slightest degree strange.

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### CHAPTER III.

#### WATER.

AQUEOUS vapour rises from the ocean, from lakes, rivers, and all collections of water upon the earth. This vapour is distributed throughout the atmosphere by the winds, and under certain conditions is again precipitated as rain, snow, &c. Besides an extremely minute quantity of saline matter, meteoric water always contains gases absorbed from the atmosphere, oxygen being, however, present in much larger proportion than in atmospheric air. All substances, therefore, which are capable of combining with oxygen, are oxidized when this water comes into contact with them.

Since the quantity of carbonic acid existing in the atmosphere is very small, meteoric water can contain but little of it. Lime-water, however, shows that it is present in it, and even in snow.\* Meteoric water absorbs this gas also from decaying vegetable mould, and being thus carried beneath the surface into the earth, it acts as a powerful decomposing agent upon rocks containing silicates of lime, protoxide of iron, &c.

The carbonate of ammonia, and the organic matter present in meteoric waters, are likewise of importance as regards their action upon rocks. The action of organic matter consists in reducing peroxide of iron (whether existing as such or in combination with silica) to protoxide. The organic matter found in the analysis of rocks is chiefly derived from the vegetable mould, whence it is extracted by meteoric water and conveyed into the rocks; but the organic matter in rocks which are not covered by vegetable mould, as in the cold zones, or above the snow level of the Alps, can only be derived from the atmosphere.

The meteoric water which penetrates rocks soon loses its oxygen and carbonic acid, when substances capable of combining with them are present in these rocks, and it also extracts from them such substances as are soluble either in it alone or by the aid of carbonic acid. These substances enable the water to effect further

\* A pupil of mine, Fabricius, upon carefully examining snow recently fallen, found that, after melting, it was rendered turbid by lime-water.

decompositions, or to give rise to new formations, on its penetrating deeper.

If, as is sometimes the case, water penetrates to greater depths than usual, and meets with large quantities of carbonic acid rising from the interior of the earth, it becomes saturated with this gas, and carbonated springs are produced.

Since meteoric water, before reaching the earth's surface, is nearly free from saline and earthy substances, while the water of springs always contains more or less of them, and since the water is continually percolating through rocks, and has done so from the most remote ages, it is evident that immense quantities of matter are continually being extracted from the earth's interior by this means. But the action of water consists not merely in forming a solution of some of the mineral substances existing in rocks, but also in producing the decomposition of silicates by the aid of the carbonic acid which it contains. This is the reason why earthy carbonates are found in the water of ordinary springs, issuing from rocks which do not actually contain these substances. The carbonic acid of these carbonates is derived wholly from the atmosphere, and from the vegetable mould through which the meteoric water percolates.

Not only do rocks lose more or less of their constituents by the action of water, they also suffer changes in their composition. The knowledge of these changes, and their laws, constitute the basis upon which chemical geology must be founded; and it is to this subject, hitherto neglected in geological investigations, that I am desirous of directing attention.

Water penetrates not only through fissures, crevices, and planes of stratification, but also through the mass of rocks. It is here necessary to distinguish the penetration of water through capillary interstices between crystalline or amorphous minerals and the rocky matrices, from the actual penetration into the minerals themselves. The larger these are, as in the coarse-grained granites, syenites, trachytes, conglomerates, &c., the more readily does water penetrate into the capillary interstices. The very fine-grained sedimentary rocks, for instance clay slate, are penetrated readily in the direction of the planes of stratification, but with difficulty in a direction at right angles to these planes. Water penetrating into crystalline minerals follows the direction of the cleavage planes.

In the shafts and adits of mines it is easy to see whether a rock is readily penetrated by water or not. The greater the obstacles presented by water in mining operations, the greater is the penetrability of the rock. In the numerous agate quarries in

the amygdaloid rock near Oberstein, the roof is always wet, water drops through everywhere and collects in the hollows. This is a fact worthy of attention in regard to the formation of agate.

When crystalline rocks whose constituents are somewhat coarse-grained are broken, the surfaces of fracture are found to be more or less moist, especially in spring. This moisture is found not only at the exterior parts of rocks, but also in the centre of blocks a foot thick and in the masses separated by blasting. This fact is most intimately connected with the durability of rocks and their value as building materials. For instance, the moister they are upon the surfaces, when broken, the less durable are they.

This porosity is by no means peculiar to coarse-grained crystalline rocks, it is also recognisable, though in a less degree, in others which are of finer texture, for instance, in basalt. It not unfrequently happens that in breaking a basalt column, moist spots may be observed here and there, even in the centre, as if small drops of rain had fallen there (p. 10). Sometimes the workmen in basalt quarries find considerable collections of water.

It is quite certain that a penetration of water into the mass of rocks must have taken place, as far as we can trace change in them, proceeding from the surface inwards. Thus in basalts, which are very liable to suffer decomposition, there are sometimes found in the interior small ochre-yellow spots which are connected with the above-mentioned moist spots; for the formation of hydrated protoxide of iron from the protoxide of the rock, necessarily presupposes the presence of oxygen and water.

Another infallible sign of the deep penetration of water into a crystalline rock of such a kind, is the effervescence caused by acids upon the surfaces of fracture quite in the interior of the mass. This is owing to the presence of carbonates formed by the combination of carbonic acid, introduced by water, with the alkaline earths or oxides of iron and manganese in the rock. The notion of carbonates, calc-spar, &c., existing as original constituents in the midst of these rocks, is one of those vague hypotheses which are by no means rare in geology. If the spots where this effervescence occurs are examined, they are found to be situated either where fine and scarcely perceptible cracks extend into the interior, or near large crystals which have capillary interstices around them, or where some traces of incipient decomposition appear. Where the rock is decayed throughout its mass, it effervesces at all parts of the fracture; a clear proof that it is especially carbonic acid which has caused this decomposition.

Rocks which, after long-continued rain, show no traces of



moisture on the fractures when broken, do not effervesce, or at least very seldom, and then only at spots near the outer surface, or where large crystals extend from thence towards the interior. Thus I found that the fractures of many pieces of phonolitic rock upon the top of Olbrück were perfectly dry, and did not effervesce, although the weather had shortly before been wet. Even the exterior surface of this rock did not effervesce, as is the case with many others, such as basalt, trachyte, dolerite, &c., which do not effervesce on the fractures. The compact character of this phonolitic rock was therefore apparent in its extreme durability.

The richness or poverty of vegetation upon crystalline rocks likewise indicates their greater or less tendency to disintegration, and, consequently, their greater or less porosity. The mountains surrounding the Lake of Laach, and consisting of volcanic scoriæ, rapilli, &c., are covered by an extremely scanty vegetation; while the neighbouring rocks, consisting of basalt or lava, are covered with the finest woods. Nevertheless, the ready penetrability of a rock cannot be unconditionally inferred from a luxuriant vegetation. Where the rocks are but little penetrable by water, nature employs another means of effecting their disintegration—the growth of moss upon the outer surfaces. This incrustation of moss gradually acquires a considerable thickness, and keeps the surfaces of the rock continually moist. Thus, where the want of porosity protects a rock from disintegration in the interior, this is effected at the surface by the moss, the moisture of which condenses atmospheric carbonic acid, and thus renders the decomposition possible. The dead moss, together with the particles of decomposed rock hanging to its roots, form a vegetable mould, and thus yield the material for a higher vegetation.

This phenomenon is very striking upon the compact doleritic rock of the Löwenburg, in the Siebengebirge. To judge from the dense wood which covers this cone to its summit, it might be supposed that the rock was very porous, and liable to decay. But if fragments are broken, the fracture is not found to be moist, or to effervesce with acids; it is only upon the exterior surfaces, covered with moss, that effervescence takes place.

A very quick and simple method of determining the greater or less porosity of a rock, is to place it in very dilute sulphuric acid in the vacuum of an air-pump. By this means, the air in the pores of the rock is removed, and on the restoration of the atmospheric pressure, is replaced the acid liquid. If, now, the piece of rock is broken after having been washed, it is easy to determine

how far the acid has penetrated by means of moistened litmus paper. When tolerably porous rocks, such as trachyte, are treated in this way, the litmus is reddened even at the depth of an inch or more. When crystalline rocks, which are acted upon by acids, are allowed to remain for months in the acid liquid, the decomposition advances generally towards the interior. This is, consequently, the most ample proof of the porosity of such a rock. Some pieces of basalt, treated in this way, were accidentally set aside, and remained untouched for some years; when the vessel was again found, the liquid had completely evaporated, and the basalt was decomposed quite to the centre. A weaker acid, as a solution of carbonic acid in water, would effect the same change, though an incomparably longer time would be necessary.

The colouring of chalcedony, which, according to Nöggerath's description, is carried on at Oberstein, shows that these siliceous substances are likewise penetrated by liquids. The colouring liquids enter the finer streaks in chalcedony which lie above one another in the agate amygdaloid.

The disintegration of many quartz rocks shows that even this compact mineral is penetrable by water; for, according to my observations, this disintegration results from the peroxidation of iron and the assimilation of water. The varieties of clay saturated with water are, like schistose rocks, the least pervious to water.

It is evident, from this description, that by far the greater number of rocks, and those which are most general, admit of the penetration of water through their substance. If it be remembered, that in the more or less deep regions from which springs of constant temperature and composition ascend, all hollows and chasms in rocks must be filled with water, it will be conceivable that even their smallest pores must be penetrated.

When we find rocks suffering decomposition in proportion as they are exposed to water, it cannot be doubted that this decomposition is most intense at the seats of the formation of mineral waters, where streams of carbonic acid issue from below, and immense quantities are absorbed under great hydrostatic pressure. Such rocks are, consequently, exposed to conditions precisely similar to immersion in dilute sulphuric or hydrochloric acid.

But even the most compact rocks, which are scarcely, if at all, permeable to water, are decomposed in the interior of the earth by the carbonic water surrounding them, in the same way as those upon the surface by the covering of moss, and the more rapidly when they are much rent.

It is on this account that springs are never found quite free from fixed constituents. If they contain but small quantities, like the thermal springs of Gastein and Pfäfers, it is a sign either that their water comes in contact with rocks which are very compact and but little liable to decomposition, containing, at the most, but a small quantity of constituents capable of becoming soluble, or that carbonic acid is absent.

We are indebted to H. Rose\* for a valuable series of investigations on the influence of water upon chemical decompositions. There is abundant evidence to show that water, in large quantities, is capable of causing the separation of substances which are united by strong affinities. Numbers of such decompositions have been long known, but that they were caused by water was either overlooked or disputed.

In the extensive class of siliceous minerals, soluble alkaline silicates are combined with the most difficultly soluble silicates of alumina, lime, magnesia, &c. The zeolites, containing water and being readily decomposable by acids, are, according to Rose,† likewise decomposed by long boiling with water when finely powdered. The soluble salts contained in some silicates, as chloride of sodium in sodalite, sulphate of soda in nosean, sulphate of lime in hauyne, carbonate of soda sometimes occurring in cancrinite, are extracted, though with difficulty, by large quantities of water, especially by boiling, but whether completely or not has not yet been ascertained. Chloride of calcium is likewise extracted from chlorapatite by large quantities of water. It is therefore evident that these minerals may be totally altered by the long-continued action of water, in consequence of the extraction of essential constituents. If the constituents of these minerals were dissolved in large quantities of water, which appears more than probable, their formation must have resulted from the complete, or nearly complete, evaporation of water; for otherwise the more soluble constituents would not have been separated. Great as is the affinity of chloride of calcium for water, its affinity for phosphate of lime must at a certain degree of concentration be still greater. It can scarcely admit of a doubt, that during long geological periods, the same effects may be produced by cold water which we are able to effect in a short time by the action of hot water.

Eighteen years ago I made some experiments as to the solubility of salts and oxides, generally regarded as insoluble.‡ In the

\* Pogg. Ann. 82, p. 545, and the following volumes.

† Loc. cit. p. 560.

‡ Journ. f. pract. Chem., t. 2, p. 73.

analysis of a mineral water extremely rich in carbonate of soda and chloride of sodium, a large quantity of distilled water was necessary for washing the residue obtained by evaporation. The water was found to have taken up (*a*) besides the more soluble salts—

	<i>a</i>	<i>b</i>
	Grains.	Grains.
Silica ... ..	0·530	0·0130
Peroxide of iron, with alumina ...	0·475	0·0380
Carbonate of lime ... ..	0·675	0·0908
Carbonate of magnesia ... ..	19·151	2·4462
	<hr/>	<hr/>
	20·831	2·5882

The solution of 28 times as much carbonate of magnesia as carbonate of lime, while the proportion of the latter to the former in the washed residue was as 5:8, shows that carbonate of magnesia is far more soluble in pure water than carbonate of lime. This induced me to digest a mixture of carbonate of magnesia, carbonate of lime, hydrated peroxide of iron and hydrated silica, in distilled water which had stood loosely covered in the laboratory for some weeks, and to allow the whole to stand several days in a closed vessel which was frequently shaken. The filtered water evaporated, and the residue examined gave the above substances in 10,000 parts (*b*). The distilled water employed might be compared with rain water, which in falling takes up probably a larger quantity of carbonic acid than this contained. This shows that pure meteoric water, while filtering through earths and rocks, dissolves quantities of substances by no means insignificant. If this fact is duly considered, it will be evident what changes the meteoric water may effect in rocks, at one place taking up substances, at another depositing them by interchange for others, and thus after millions of years, producing results which excite our astonishment, although the means by which they are brought about are apparently so unimportant that they are mostly overlooked. In this action lies the whole secret of the production of pseudomorphs, as was shown in Chap. II.

W. B. and R. E. Rogers\* found that water saturated with carbonic acid, and even pure water, partially decomposed and dissolved the following minerals and rocks:—

\* These experiments are extracted from a copy of the author's paper published in the American Journal of Science and Arts. 1848.



Soda felspar.	Hornblende.	Talc.
Potash felspar.	Grammatite.	Steatite.
Lithia felspar.	Asbestos.	Chlorite.
Glassy felspar.	Olivine.	Serpentine.
Labrador.	Chalcedony.	Obsidian.
Mica.	Epidote.	Lava.
Lencite.	Analcime.	Greenstone.
Tourmaline.	Mesotype.	Gneiss.
Angite.	Skolezite.	Hornblende slate.*
Kockolite.	Axinite.	
Hyperstene.	Prehnite.	

The finely powdered minerals were washed with distilled water upon a filter of paper previously freed from all substances soluble in water, and the filtrate tested. At the same time the powder was from time to time shaken with water and the filtrate evaporated to dryness. Both operations were carried on as well with pure water free from air as with water containing carbonic acid. When the mineral was very finely powdered before being washed, the first drops generally showed traces of alkalies or alkaline earths. The action of carbonated water was recognisable in less than ten minutes, and by returning the filtrate the effect was increased. With pure water the effect was much weaker and required a long time, but it was perfectly decisive with almost all the above mentioned minerals, and with some it was considerable. The presence of alkalies, lime, or magnesia could be recognised in a single drop of the filtrate. By continued digestion of the powdered minerals with carbonated water for 48 hours, and with pure water for a week, sufficient quantities were sometimes dissolved for quantitative analysis. Thus from felspar, hornblende, grammatite, epidote, mesotype, chlorite, serpentine, &c., so much silica, alkalies, lime, magnesia, peroxide of iron and alumina were obtained, that they amounted to 0·4 or 1·0 per cent. of the mineral. The alkalies and alkaline earths were obtained as carbonates, the iron from hornblende and epidote passed from carbonate into hydrated peroxide during the evaporation.

Most of the minerals mentioned, when powdered in a chalcedony mortar and moistened with pure water, in a platinum crucible, showed an alkaline reaction with litmus paper, and especially felspar, mica, hornblende, grammatite, asbestos, chlorite, serpentine.† It is deserving of notice that this reaction is quicker and

\* Different kinds of glass, Chinese porcelain, and Wedgewood-ware are also acted upon.

† The authors state that powdered glass shows this reaction with remarkable distinctness. Some considerable time since (Kastner's Archiv., 1824, t. 1, p. 442), I found that the powder obtained by filing glass, produced a striking alkaline taste when placed upon the tongue.

stronger in silicates of magnesia, or of lime and magnesia, than in felspar and most other alkaline minerals. The proportionally easier decomposition of these silicates by carbonated, and even by pure water, explains, as the authors remark, the rapid decomposition of rocks which consist principally of hornblende, epidote, chlorite, &c.

Wöhler's\* very interesting experiment of dissolving apophyllite in water, and reproducing it from the solution in crystals, shows that a mineral may be dissolved without any decomposition (p. 31). It is true that this solution was only effected by very hot water, and, according to Bunsen, cold water has not the least action; but as the Messrs. Rogers have succeeded in dissolving similar zeolites, and other minerals, although their solubility was less to be expected, it seems scarcely probable that cold water exerts no solvent action upon apophyllite. But without special experiments, this question cannot be decided. This solubility of apophyllite without decomposition explains the formation of this mineral in fissures and drusy cavities. It is not improbable that other zeolites will exhibit the same behaviour.

Whatever change water causes in finely powdered minerals, during a short time, must also be produced, though more slowly, when it comes in contact with larger fragments or whole crystals. The only difference is, that the surfaces of contact are diminished the larger the masses are.

The chromatic phenomena observed between glass plates very nearly in contact, admit of the calculation of extremely small interstices. Newton determined the smallest space which gave a white colour, at something more than  $\frac{1}{14000}$  line; and Haüy has calculated, from the various refraction of mica, that the thickness of a plate of mica which caused the same effect as this film of air, is  $\frac{1}{900000}$  line.† If a cube of mica, whose edges are one inch in length, be split into plates of this thickness, the surface of contact of the whole would be 150,000 square feet. Let us suppose that a mineral is so finely powdered, that each particle, which, for the sake of simplicity, we will suppose to be cubes, are as thick as these plates, having edges  $\frac{1}{900000}$  line in length, then the number of particles which a cube of one inch would give is—

$$900,000^3 \cdot 1728 = 1,259,712,000,000,000,000.$$

It is very doubtful whether such a degree of subdivision can be effected by mechanical means, *i.e.* by trituration in a mortar; but we will assume that it can, for the sake of argument. The entire

\* Jahresbericht, by Liebig and Kopp. 1847 and 1848, p. 1262.

† Pogg. Ann., t. 24, p. 25.

surface of these particles would then be  $3 \cdot 150,000 = 450,000$  square feet, *i.e.* a square of 670 feet lateral dimensions. Since, now, one cubic inch has a surface of six square inches, its proportion to the surface of these particles is as—

$$6 : 64,800,000 = 1 : 10,800,000.$$

It is probably admissible to assume that the time in which water produces similar effects of decomposition or solution on minerals, is inversely as the magnitude of the surfaces of contact. If, therefore, a mineral were so far subdivided that the surface was increased ten million-fold, the quantity then dissolved during a certain time, would be the same as that dissolved during a period ten millions as long when the undivided mass was acted upon.

The Messrs. Rogers found that when 40 grains of finely powdered hornblende were digested for forty-eight hours with carbonated water, the quantity of silica, peroxide of iron, lime, and magnesia dissolved was 0.355 grains. By repeating this treatment 112 times with fresh carbonated water, under otherwise similar circumstances, a perfect solution would be effected. This would require a time of 224 days. If now 40 grains of hornblende unpowdered, in which, according to the above assumption, the surface is only  $\frac{1}{10000000}$  of the powdered, were treated in the same way, and the water renewed every two days, the time required for perfect solution would be 2,240 million days, or somewhat more than six million years.

When the chemist treats a substance with water, but cannot detect its presence in the water either by reagents or by evaporation, he regards it as insoluble. But this is by no means a proof of its absolute insolubility, for the action of reagents is no longer perceptible in high degrees of dilution, and the residue left on evaporation may be so slight that it is no longer recognisable. But when one mineral is found in the form of another, whose solubility cannot be recognised by chemical means, this is an evidence that water has acted upon the displaced mineral for, perhaps, many hundred thousand years, and gradually dissolved and removed it. I have already shown what an important part water plays in all pseudomorphic processes (p. 41).

In attempting to estimate the time occupied by processes going on in the mineral kingdom, we arrive in this case, as in all others, at enormous periods. The six million years required for the solution of hornblende is again lengthened, if the quantity of water coming in contact with the crystal imbedded in a rock is less than that assumed in our calculation. On the other hand, it

must be remembered that no mineral, and least of all, the readily cleavable, frequently cracked and porous hornblende, is perfectly impervious to water. But if water penetrates through the planes of cleavage into the interior of the minerals, then the case is altered by the increase of the surfaces of contact, and the solution takes place in a much shorter time when, at least, the water has unimpeded access. We may, therefore, understand why the time required for the formation of displacement-pseudomorphs in rocks which are but slightly pervious, and which are exposed only to the action of meteoric water filtering through them, is far longer than in fissures through which water passes, or at the bottom of rivers, seas, or lakes, where the minerals are continually acted upon. The metamorphoses of rocks, which have laid for ages in these positions, are, therefore, not in the least to be wondered at.

All evidence, then, proves that those minerals whose constituents are not decomposed by the atmosphere, and suffer no alteration from this source, still are not capable of resisting the solvent action of water. The mineral kingdom, therefore, contains nothing which is unchangeable, unless, perhaps, it be the noble metals, gold and platinum.

Water is present, chemically combined, in many minerals, and especially in the zeolites. Water plays an important part in the mechanical disintegration of rocks. The expansion of water in freezing is one of the most energetic causes. After the thawing of ice in fissures and pores of rocks, immense masses are dislodged from the declivities. This phenomenon is the more considerable in the Alps, since it is not limited only to particular seasons, but is of almost daily occurrence in the higher regions. The upper part of narrow ridges of rock often consist of a series of large angular fragments, which still occupy the place of the former solid rock, but are only loosely situated one above the other.\*

Rivers having a considerable fall, undermine rocky masses, and cause them to fall. They deepen their beds more considerably in proportion to their fall. Consequently, this is more especially the case in the higher parts of their course than lower down and near their entrance into the sea, where the fall is inconsiderable. During freshets, a river tends chiefly to widen its course, without greatly deepening it. The Falls of Niagara afford a magnificent example of the progressive excavation of a deep valley in solid rock. It has long been the popular belief that this river once flowed in a shallow

\* Herman and Adolph Schlagintweit, *Untersuchungen über die physikalische Geographie der Alpen*. 1850, p. 308.



valley, from the present site of the falls to an escarpment called the Queenstown Heights. It is supposed that at this escarpment the cataract was first situated, and that the river has been slowly eating its way backwards through the rocks, for the distance of seven miles. This hypothesis naturally suggests itself to every observer, who sees the narrowness of the gorge at its termination.

Lyell,\* after the most careful inquiries made during his visit to the Cataract in 1841-2, came to the conclusion that it recedes one foot, upon an average, annually. In that case it would have required 35,000 years for the retreat of the falls from the escarpment of Queenstown to their present site. It seems by no means improbable that such a result would be no exaggeration of the truth, although we cannot assume that the retrograde movement has been uniform.

At the Falls of Niagara, strata of limestone lie upon slate beds. The rushing of water occasions violent gusts of wind, charged with water, to be driven against the slate-shale. The continued action of these water-charged whirlwinds displaces the shale and throws it down in a talus. From the removal of this shale, the superincumbent limestone loses its support and falls.

The transport of detritus by rivers, and even in Alpine rivers, proceeds but slowly, notwithstanding the great velocity of the latter. It requires a frequently repeated impulse and a long time in order to carry the masses of rock to a distance of many miles. Extraordinary floods, such as that which occurred in Banienthal (Val de Bagnes), in Unter-Wallis, on the 16th of June, 1818, are certainly attended by extraordinary effects. Below the narrow gorge of Lortier, the enormous mass of water is said to have driven a mountain of detritus, of a height scarcely credible, of more than 300 feet; granite blocks, of nearly 1000 cubic feet contents, are even still forced to a distance of 1800 feet by water, near Martinach. As the mean velocity of this flood was 33 feet per second, while that of the rapid Alpine streams very seldom exceeds 13 feet, and as its quantity of water was five times as great as that of the Rhine at Basle, when it is high,† the transport of detritus by this extraordinary flood cannot serve as a criterion of what the Alpine streams are capable of effecting in their normal state.

But even the effects of the flood of Banienthal are not suffi-

\* Principles of Geology. Seventh ed., p. 202, et seq.

† Bischof Populäre Briefe über die gesammten Gebiete der Naturwissenschaften. 1848, t. 1, p. 243.

cient to justify the assumption, that the erratic blocks which are frequently found at considerable heights upon the declivity of the mountains opposite the Alpine valleys, for instance, upon the Jura, opposite the valley of the Rhone, have been carried so far from their source by such floods breaking out from the centre of the Alps. Such an assumption meets with no support in the fact of the transport of granite blocks at Martinach, for it was not the water, but the immense quantity of wood which was carried along with it, that rolled away these blocks along the bottom of the stream. Finally, the assumption that large blocks would only sink gradually in a mass entirely filled with detritus and mud,\* is inconsistent with physical laws; for if this were the case, the quantity of the detritus must be so great in proportion to that of the water, that the whole would be more a solid than a fluid mass. But such a mass would move forwards but slowly, and the large blocks would have sufficient time to sink before reaching the opposite declivity of mountains.

The attrition of the rocks upon the banks and beds of rivers is especially favoured by the suspended particles which they contain; for they strike the rock with the velocity communicated by the stream. In Chapter VIII., we shall see that the Alpine rivers are characterized, before their discharge into the lakes, by the great quantity of suspended matter.

Landslips are caused by the mechanical action of water. An argillaceous substratum will get gradually moist at the surface, and in favourable situations may become a wet clay. The stability of the mass above will depend upon the relative position of the strata. Thus, if on a mountain water penetrates through an inclined porous strata to an impervious clay bed, the surface of the latter would become slippery, and the mass above be launched into the valley. Now this is precisely what happened on the 2nd of September, 1806, at the Ruffiberg, or Rossberg, in Switzerland, which is 5,196 feet above the level of the sea. Its upper part is composed of porous beds of a compound rock formed from the *debris* of the Alps, and rests upon a clay stratum; the whole dipping at an angle of 45°. The clay becoming soft by the action of the water, and the thick superincumbent beds losing their support, the latter were launched over the slippery and inclined surface beneath, and the valley below was covered with their ruin.

Large falls from mountains take place from the percolation of

\* Bischof, Populäre Briefe über die gesammten Gebiete der Naturwissenschaften. 1848, t. 1, p. 252.

water to certain portions which they mechanically loosen or chemically destroy without sliding over an inclined plane, though the force of gravity still causes the fall. The Alps have afforded many examples of this fact; among others, those of the great falls from the Diablerets, in 1714 and 1749,\* and from the Gemmi. The foot of the latter mountain consists of a clay slate, which is very readily disintegrated by the mechanical action of water. Upon the bank of the Dala I observed how this glacier stream had deeply corroded the clay slate which forms the basis of the Gemmi, so that the superincumbent beds of limestone hung over. When these beds lose their support, falls ensue. The landslips at the Diablerets were likewise caused by the displacement of the clay slate lying under the limestone.

De la Beche† alludes to the under cliffs at Pinchay, near Lyme Regis, as an example of the destruction of a cliff by means of land springs, greater than that which is produced by the action of the sea at the same place. Water percolates through the chalk and greensand to the clay; being here arrested in its progress downwards, it escapes by the easiest road, which is that presented by the cliff originally formed by the sea. It here gradually carries away the clay, the chalk and greensand lose their support, give way, and fall over into the sea.

The mechanical action of water is very variable, even upon the same rocks. This results, partly, from an unequal porosity; partly, in sedimentary rocks, from the varying nature of the cementing matter. Thus it happens that, in a separate sandstone rock, parts are carried away by water, others are less acted upon and remain unchangeable, and in remarkable forms, as in the so-called rock labyrinth at Adersbach, in Bohemia, the Externstones, near Meinberg, in Lippe Detmold,‡ and Saxon Switzerland show.

The detritus of rocks is more or less abundantly carried down by avalanches of snow; they are great transporters of such fragments. When thus thrown upon glaciers, they are carried forwards by the latter. In front of glaciers there is usually a very considerable pile of rubbish, composed of pieces of rock and earth (moraines, gandecken), which they have forced forward. The motion of glaciers produces immense effects. At their sides and under surface, rocks are shattered by the enormous pressure of the advance-

\* A Geological Manual by H. de la Beche. London, 1831, pp. 44 and 45.

† Ibid., p. 46.

‡ Bischof, Populäre Briefe. T. 1, p. 70, et seq.

ing masses of ice, several hundred feet thick, and their surfaces left smooth and polished. The fragments separated at the side mix with the ice of glaciers; those rubbed off by the under surface render the glacier streams muddy.

Breakers are continual and powerful agents of destruction of coasts in some situations, while in others they pile up barriers against themselves. Their destructive influence is principally felt when the rocks on which they are discharged are composed of soft materials, and rise somewhat abruptly above the level of the sea. The destruction of coasts of equal hardness almost always bears a proportion to the extent of open sea to which such coasts are exposed. The configuration of most coasts will be seen to be determined by the hardness of the rocks composing them; the softer strata giving way before the battering power of the breakers, while the harder rocks preserve their places for a greater length of time. If the rocks which form a coast be stratified, much depends upon the dip of the strata relatively to the breakers. Thus, in many situations on the southern coasts of Devon and Cornwall, the slaty rocks dip in such a manner towards the sea, that the waves have never effected more than the removal of some loose superficial matter. The destructive power in other situations is well known; and of this, the eastern coast of England presents abundant proof, where very considerable encroachments of the sea have been recorded within the lapse of a few centuries. The substances so forced away by the action of the breakers, will be acted on according to their weight, form, and solidity. The tides will remove so much of them as they are able to transport, and the rest will remain on the shore within the immediate influence of the breakers, which constantly tend to grind them down into smaller portions, and finally into sand.

In the destruction of a cliff of unequal hardness, it not unfrequently happens that the harder portions, when large, such as many concretions in sandstones and marls, or blocks of indurated strata, remain at the base of the cliff, and in a great measure protect it from the more powerful effects of the breakers.\* In this case the waves produce the same effects as rivers and springs above mentioned.

Veins of one substance, or rock, traversing another are generally of different texture and solidity from that which they cut, and consequently nothing is more frequent on sea shores than to

\* De la Beche, loc. cit. p. 70.



observe them either standing out in relief or hollowed into caves.\* This phenomenon likewise finds its analogy in the clay slate detritus with quartz veins, which sometimes project for several lines beyond the rock.

When a shingle beach is partly torn up, and held in temporary mechanical suspension by the breakers during a heavy gale, the action of the waves is very considerable, even on the hardest rocks, so as to scoop them out near the ordinary level of the sea. In exposed situations the hardest rocks are often drilled into holes or caverns, from the force of the broken wave being driven, by local circumstances, more in one direction than another, or from the inferior hardness of different portions of the rock. The most beautiful of ocean caverns, Fingal's Cave, in Staffa, owes its existence to the circumstance of the basaltic columns being jointed in that place, while the general character is to be without divisions in the columns.†

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## CHAPTER IV.

### SPRINGS.

METEORIC water penetrates, more or less, into the earth in proportion to the permeability of the surface upon which it falls. The water which has penetrated to a certain depth, either reappears as springs at lower levels, or continues its subterranean course to neighbouring rivers, lakes, or seas. However simple the course of water upon the surface of the earth may be, its subterranean course is sometimes very complicated, as is sufficiently shown by the position of many springs.

The facts ascertained in mining operations, the knowledge acquired by geognostic investigation as to the character and alternation of rock formations, the observations of the temperature of springs, the phenomena of artesian wells, &c., have thrown so much light upon the origin of springs that there remains but little which is hypothetical in the theory of them.‡

\* De la Beche, *loc. cit.*, p. 71.

† Macculloch, *Western Islands of Scotland*.

‡ In the German edition, the origin, subterranean course, locality, and temperature of springs have been treated of at length (Vol. 1, p. 7-223). In this

All springs derive their origin from meteoric water—rain, snow, dew, &c.—the water of brooks, rivers, lakes, and seas, and the melted ice of glaciers.

*A.—Springs which originate from rivers.*

When valleys are filled with detritus, this is saturated with water from the rivers flowing through them as far as the river level. If, therefore, a shaft is sunk in the detritus to this depth, the water below rises in it. Such a shaft is an ordinary well. The water rises and falls in it in the same degree as in the river. The detritus is consequently exposed to the uninterrupted influence of water, which dissolves or decomposes whatever substances it meets with capable of undergoing such changes.

It is well known that water may be obtained by sinking wells in solid rocks above the river valleys, and even upon mountains, if the rock is permeable by water. In such wells the water originates solely in the accumulation of meteoric water which has penetrated into the rock.

*B.—Springs originating in the water which sinks through the beds of brooks and rivers.*

When the surface over which rivers flow is very much fissured, as is especially the case in limestone formations, much larger quantities of water sink into the earth than when it consists of detritus. If this fissured stratum has a great thickness, and there is no second impermeable bed within a considerable depth, the quantity of water which sinks is so great that the river will finally be exhausted.

If the fissured stratum is surrounded on all sides by impervious strata, the sinking of the river water will cease as soon as all the fissures are filled. But if, on the contrary, the fissured stratum again appears at the surface at a lower level, the sunken water will flow out here, and will be replaced in the same proportion in the fissures by the water of the river.

The greater the quantity of water in the river, the further will it flow over the fissured surface before sinking entirely. It is on this account that, in the spring, or after heavy rains, the point of total disappearance advances, and during dry weather recedes. In the former case all the fissures are filled up to the level of the edition I have confined myself to the consideration of those points only which refer to the chemical and mechanical changes in rocks which result from the subterranean circulation of water.

water in the river; in which case the fissured stratum can only take up as much water as flows out where this stratum again appears at the surface. During dry weather, on the contrary, when more water flows from this stratum than flows into it, the water sinks in the fissures, and it may then be heard at the banks of the river falling into them. When the fall of a river is great, and the motion of the water over the fissures consequently more rapid, less water is lost; but when the motion is slow, it disappears more quickly.

The point of total disappearance of such a river is, therefore, determined by the weather; the dryer it is, the more does this point approach the source of the river; and the wetter it is, the more does it recede from its source.

These phenomena present themselves, among others, in a very striking manner upon the western declivity of the Teutoburger Wald, and upon the northern declivity of the Haar.\*

When the surface consists of strata which are very much fissured, such as chalk, chalk marl, and greensand, almost all the meteoric water penetrates to a depth where it meets with an impervious stratum. In such situations there are no springs, and no water can be obtained by sinking wells unless they reach as far as this impervious stratum. It is only when partially impervious strata here and there intersect such fissured rocks that scanty springs, and wells poor in water, can possibly exist.

The phenomenon of periodic springs is not unfrequent in fissured rocks. These springs flow when the water is high in the fissures and clefts, but cease as soon as the water sinks below a certain level. If such springs communicate with a contiguous brook, the singular phenomenon presents itself of the water flowing, in the first case, into the brook; and in the second case, the brook water flowing into the dry springs and disappearing.†

When the rocks are very much fissured, the greater part of the rain and snow water penetrates into them, and very little flows away over the surface; but when, on the contrary, they are not much fissured, very little water penetrates, and more flows over the surface. But the more water penetrates a rock, the greater is the quantity of matter removed mechanically and chemically.

Among the rocks which constitute large formations, it is espe-

\* G. Bischof, on the remarkable characters of the springs on the western declivity of the Teutoburger Wald. *Neues Jahrbuch der Chemie u. Physik.* Vol. 8, p. 249 et seq.

† Bischof, German edition, Vol. 1, p. 18.

cially the limestones, which are dissolved in large quantities by water. Much is also carried away from them mechanically by water, as is shown by the great turbidity of rivers flowing through these rocks, and of many springs issuing from them, after heavy rains. It is on this account that landslips and caves occur most frequently and on the largest scale in these rocks. The former I found, as funnel-shaped depressions, abundant upon the elevated plains of the Teutoburger Wald and the Haar, as well as upon the Gemmi in Switzerland. They are also very numerous in the limestone mountains of Krain, and in the northern part of the chalk formation of Denmark.\*

From the quantity of water of the rivers of the Teutoburger Wald and the Haar, and the quantity of carbonate of lime which they contain, I have calculated that a quantity of this substance is annually extracted from these mountains, amounting to far more than a cube of 100 feet lateral dimensions. One of the largest earth-falls forms an inverted cone of about 150 feet diameter and 25 feet depth. The Pader springs alone would remove such a cone of carbonate of lime in solution in about 67 days.

These immense quantities of carbonate of lime, which the rivers in that district abstract from the chalk-marl rocks, are quite sufficient for the explanation of the earth-falls which have occurred and are daily occurring there.

The first occasion of these earth-falls is undoubtedly to be sought in the caves of the limestone rocks. In wet weather, these caves are completely filled with water, which, acting both chemically and mechanically, ultimately causes the falling in of the roof, and thus causes the sinking of the blocks of limestone divided by the fissures. It is for this reason that earth-falls are frequently the result of long-continued rain. Sometimes, however, they are again filled up.

The circumstance that the sinking rivers in fissured rocks have a variable temperature, while the springs which originate from them have a temperature which is either constant or varies only within very narrow limits, can only be explained by assuming the existence of immense subterranean collections of water. There must, therefore, be numerous caves filled with water in the limestone mountains. I have calculated that these buried masses of water in the Teutoburger Wald, must be about equal to a lake 120 feet deep.†

\* Forchhammer, in Pogg. Ann. Vol. 58, p. 611.

† Bischof, German edition, Vol. 1, p. 108.



When mining operations are carried on in fissured mountains, and the water flows away through adits, or is pumped up, it frequently happens that the springs and wells, within a considerable distance, are drained of their water, and sometimes dried up entirely.

*C.—Springs which originate from elevated lakes.*

In elevated lakes, which have an abundant supply of water, and but a limited discharge, the water escapes by subterranean channels, a circumstance which indicates that the bottoms of these lakes consist of fissured rocks. If they are of limestone, considerable quantities of matter are washed away, giving rise to the formation of caves, and finally of earth-falls.

Such phenomena occur very markedly upon the Gemmi. About 7000 feet above the level of the sea, lies the Daubensee,  $2\frac{1}{2}$  miles\* in length, which has no visible discharge, although the considerable glacier stream, from the great Lammern glacier, falls into it, as well as all the rain and snow water of the surrounding mountains. About 1200 feet lower, at the Spital-Matte, between Kanderstäg and the Gemmi, more than fifty very copious springs issue, and by their junction form a not inconsiderable brook. It is very probable that these springs originate from the Daubensee, for the bed of this lake, and the entire Gemmi, consist of limestone which is very much fissured. The appearance of the blocks of limestone, irregularly piled above each other, and from which these springs issue, seem to warrant the assumption of very considerable excavations by water.

The Lac Glace d'Or, in the valley of Larboust, in the Pyrenees, 8166 feet above the level of the sea, likewise gives rise to a considerable spring.† The abundant spring of the Orbe, in the Vallorbe valley, in the Jura mountains, also originates from an elevated lake.‡

*D.—Springs are formed by the melting of the snow and ice of glaciers.*

If the surface upon which a glacier rests, consists of a rock which is permeable to water, such as fissured limestone, water sinks through these fissures, and after a subterranean course,

\* The miles in this work are always sea miles ; 60 = 1° of the equator.

† Charpentier. Essai sur les glaciers. Lausanne, 1841, p. 93.

‡ Ibid., p. 279.

again comes to the surface, in springs, below the level of the glacier. On this account, numerous and abundant springs are found in the valleys below glaciers.

If these springs originate solely in the ice which melts upon the surface of the glacier during warm weather, they flow only as long as this continues, and are quite dry in winter. In this way periodic springs are formed. But if these springs are supplied with water from other sources, which continue during the winter, they flow in this season, although less abundantly.

If we reflect what immense quantities of water the glacier streams carry off, it is easy to conceive what extensive excavations must take place in rocks which support glaciers; and also in the rocks under ground through which the water flows. I have, in the German edition, mentioned several examples of springs in Alpine mountains, which undoubtedly originate in glaciers.\*

#### E.—*Mountain Springs.*

The number of springs which issue on the declivities, or at the foot of mountains, and their relative abundance of water, indicate the degree of penetrability of the rock by water. These springs are called mountain springs; their constituents indicate what substances have been extracted from the rocks.

The meteoric water filters through these rocks more or less quickly in proportion to their permeability. But the solvent and decomposing effect of the water is greater in proportion to the slowness with which this filtration goes on. These phenomena are most evident in mines. If the descent of water is not prevented by impervious strata, it is seen to drop from fissures, and from the rocks throughout the mine. This water accumulates to such a degree, that it is necessary to remove it continually by pumping.

#### F.—*Springs which rise from great depths.*

These springs are remarkable, not only because the cause of their ascent was so long a mystery, and was not discovered until very recently, but also because they come to the surface with a high temperature, and frequently with larger quantities of mineral substances than other springs.

The ascending springs indicate an alternation of strata which

\* Vol. 1, p. 33, et seq.

are permeable, with others which are impermeable by water, and an inclination in their position.\* The impermeable strata may be regarded in the light of tubes which inclose the water circulating in the permeable strata. The ascent of springs takes place altogether in accordance with the laws of hydraulics. Ascending springs can occur, for the most part, only in sedimentary rocks, although there are instances of such springs in crystalline rocks. They very frequently make their appearance at the boundaries of crystalline and sedimentary rocks.† The water pressure may be exerted miles distant from the spot where the springs ascend. It is well known that ascending springs may be formed artificially (artesian wells), by carrying borings down to permeable strata, which are inclosed by others which are impervious.

Ascending springs are generally much more abundant in water than mountain springs, for they originate in more or less considerable subterranean collections of water, and ascend more rapidly the greater the pressure to which they are exposed. If, in the interior of the earth, they come into contact with streams of carbonic acid, this gas is absorbed, and carbonated springs are formed. The greater the depths from which they come, the higher is their temperature. All these circumstances together contribute to render these springs richer in mineral constituents than the mountain springs. They therefore extract more from the rocks than mountain springs.

The solutions and decompositions by which mineral substances are introduced into the water of springs, take place at the depths where the accumulations of water, in which ascending springs originate, are situated. The sides of the channels through which these springs ascend, are acted upon, when they contain soluble and decomposable minerals, as far as the water penetrates.

The effects produced by ascending springs upon rocks are, then, quite different from those produced by the meteoric water filtering through them. This water penetrates the entire rock in so far as it is penetrable, and all rocks are so to some extent; it, therefore, everywhere exerts a solvent and decomposing action. The substances which have been dissolved, may be again deposited in drusy cavities and fissures, when the necessary conditions are present. It is, therefore, the water which filters through rocks whose solvent and decomposing action extends throughout whole mountains.

\* The subject of ascending springs is fully treated of in the German edition. Vol. 1, p. 40, et seq.

† Forbes, in Phil. Trans. Vol. 2 for 1836, p. 575.

Up to the present time, the following substances have been found in springs, well-waters, salt brines, sea water, &c. :—

1. Saline bases : soda, potash, lithia, ammonia, lime, magnesia, strontia, baryta, alumina, protoxides of iron and manganese, oxides of zinc and copper, tin, lead, silver, antimony, arsenic, nickel, cobalt, probably also as oxides.

2. Acids : carbonic, sulphuric, sulphurous, nitric, phosphoric, boracic, silicic, hydrosulphuric.

3. Halogens and metaloids : chlorine, bromine, iodine, fluorine, sulphur, hydrogen.

4. Organic substances : extractive matter (baregin), crenic acid and apocrenic acid.

The presence of oxygen and nitrogen in the water of springs has already been treated of. Sometimes, also, carburetted hydrogen is evolved from springs, and exists, therefore, in solution in their water.

According to the length of time that water remains in contact with rocks which contain salts or soluble substances, more or less of these are extracted, and such a solution may go on even to saturation. Chloride of sodium and sulphate of lime are the only substances with which water is sometimes saturated, when it penetrates into beds of rock-salt or beds containing gypsum. In other springs, which are likewise formed by a simple process of solution, chloride of sodium, which is seldom entirely absent, occurs in much smaller quantity.

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## CHAPTER V.

## RIVERS.

THE mineral constituents of springs are likewise found in rivers and brooks. They are, however, subject to great variations in quantity. During dry weather, and when the ground is covered with snow and ice, the rivers receive their supply of water from springs only; the quantity of mineral constituents in rivers is then the greatest. In wet weather, on the contrary, when the rain and snow water amount to far more than the water yielded by springs, the quantity of mineral constituents decrease; for this water, flowing rapidly and in large quantity over the surface, dissolves much less than the water which penetrates through the rocks; but then this water conveys more or less suspended matter into the rivers, rendering them turbid.\* This subject will be treated of in Chapter VIII.

I have arranged together in the accompanying table all the analyses of river waters with which I am acquainted. The quantity of the several constituents is in all cases calculated for 100,000 parts of water.

\* On this account, a single analysis of a river water at a certain time of the year does not admit of a calculation being made of the quantity of matter which reaches the sea in a state of solution in rivers, even when the mean annual quantity of water conveyed into it by them is known. Everest (Lyell's Principles, 7th ed., p. 269) found that, in 1831, the number of cubic feet of water discharged by the Ganges per second was, during—

The rains (4 months)	...	...	494,208
Winter (5 months)	...	...	71,200
Hot weather (3 months)	...	...	36,330

If the water of the Ganges during these three periods were analysed, it would be possible to estimate the quantity of matter conveyed into the sea in a state of solution by this great stream.

It is much to be desired that future analyses of river waters should, at least, be made when the water is at the highest or lowest level, so as to be applicable to the determination of the quantity of dissolved matter conveyed into the sea by these rivers.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
	Rhine, near Basle, (Autumn)	Rhine, near Strasbourg	Rhine, near Bonn, (March, 1851)	Rhine, near Bonn, (March, 1852)	Daube, near Vienna, (August, 1852)	Elbe, near Hamburg, (June, 1852)	Maes, near Hocht.	Maes, near Boelolt.	Maes, near Pierre-Blanc.	Maes, near Arendonck.	Rhone, near Geneva, (April)	Rhone, near Lyons, (July)	Rhone, near Lyons, (February)	Lake of Geneva.	Garonne, near Toulouse, (July)	Loire, near Orleans.	Seine, near Berry, (June)	Seine, above Paris.	Thames, near Greenwich, (January)	Thames, near Twicken- ham, (December)	Thames, near London Bridge, (October, 1848)	Thames, at Ditton.	Thames, near Kew.	Thames, near Barnes.	Thames, near Red-house, Battersea.
Carbonate of lime	12.79	13.56	3.24	9.46	8.37	6.98	13.69	12.55	4.98	3.21	7.69	10.00	15.00	7.2	6.45	4.81	16.85	11.3	20.54	18.23	11.56	6.84	15.57	14.30	13.25
" of magnesia	1.35	0.50	1.22	0.65	1.50	0.59	2.70	2.41	0.89	0.55	0.49	...	...	0.7	0.34	0.61	0.27	0.4	1.13	0.39	0.18	1.81	1.67	1.66	1.54
Silica	0.21	4.88	2.05	0.89	0.49	0.54	2.00	1.82	1.04	0.38	2.38	trace	...	0.1	4.01	4.06	2.44	0.5	0.13	0.39	0.08	0.89	0.63	1.43	1.01
Peroxide of iron	trace	0.58	0.69	0.28	0.20	...	0.50	0.50	0.24	0.23	0.39	...	...	...	0.31	0.55	0.25	...	trace	trace	0.13	0.96	1.09	0.41	0.0
Alumina	trace	0.25	0.10	...	...	0.12	...	...	...	0.23	0.59	...	...	...	0.30	0.71	0.05	...	trace	trace	0.13	0.96	1.09	0.41	0.0
Sulphate of lime	1.54	1.47	...	2.38	0.29	0.72	1.22	1.36	2.03	1.24	4.66	0.60	2.00	2.6	...	0.71	0.05	3.6	9.54	3.70	4.56	4.37	4.66	6.83	8.01
" of potash	0.39	...	...	1.81	1.87	...	0.43	0.30	0.21	0.12	0.63	trace	0.70	3.1	...	...	0.269	0.6	2.85	0.95	0.24	0.87	0.69	...	...
" of soda	0.18	1.35	...	0.16	0.20	...	...	...	...	...	0.74	...	...	...	0.53	0.34	1.23	0.50	1.36	0.95	0.24	0.87	0.69	...	...
Chloride of sodium	0.15	0.20	3.89	1.45	traces	3.94	1.50	1.40	1.00	0.92	0.17	trace	0.70	...	0.32	0.48	...	...	4.44	2.34	1.57	2.00	2.69	...	...
" of potassium	...	...	...	...	...	...	...	...	...	...	...	trace	...	...	0.32	0.48	...	...	0.21	0.34	0.85	1.57	2.00	2.69	...
" of calcium	...	...	...	...	...	...	...	...	...	...	...	trace	...	...	0.32	0.48	...	...	0.21	0.34	0.85	1.57	2.00	2.69	...
Carbonate of soda	...	...	...	...	...	...	...	...	...	...	...	trace	...	...	0.32	0.48	...	...	0.21	0.34	0.85	1.57	2.00	2.69	...
Silicate of soda	...	...	...	...	...	...	...	...	...	...	...	trace	...	...	0.32	0.48	...	...	0.21	0.34	0.85	1.57	2.00	2.69	...
Nitrates	...	...	...	...	...	...	...	...	...	...	...	trace	...	...	0.32	0.48	...	...	0.21	0.34	0.85	1.57	2.00	2.69	...
Organic matter	0.33	0.38	...	...	...	...	...	...	...	...	0.65	...	...	0.9	0.65	1.46	...	1.0	...	...	0.39	0.87	0.69	...	...
	...	...	...	...	...	...	...	...	...	...	0.65	...	...	0.6	0.44	0.44	1.46	trace	5.92	4.97	10.00	8.27	4.39	3.93	3.40
According to direct determination	16.94	33.17	11.23	17.08	12.42	12.69	22.04	20.34	10.39	6.55	18.20	10.60	18.40	15.2	13.67	18.46	25.24	18.2	39.79	32.05	36.52	30.47	31.01	32.45	30.52
Suspended matter	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	32.13	...	29.69	31.03	32.39	30.40
	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	0.01	0.03	...

[illegible]

1. Paggenstecher. Physical, chemical, and geological researches on the internal heat of the globe, by G. Bischof, vol. i. p. 84.

2. Deville. *Ann. de chim. et de phys.* t. 1848, xxiii. p. 32.

3. Bischof. The Rhine was much swollen and very turbid at the time this water was taken. The substances soluble in pure water were not examined, but merely their total weight estimated.

4. Bischof. The Rhine was very low and the water of the usual clearness.

5. Bischof. The Danube was tolerably clear, the water level two feet above zero, the temperature of the water 72° F. The difference between the direct determination and the sum of the constituents, is to be ascribed chiefly to organic substances which were not determined directly. The carbonate of lime showed distinct traces of strontia. Alkalies could not be detected: the sulphates of the alkalies mentioned, proceeded from the excess of sulphuric acid. The minute quantity of chloride of silver precipitated was accidentally lost.

6. Bischof. The Elbe was turbid, the water level 7¼ feet, wind west. The temperature of the water 59° F. Half an hour before the water was taken, the tide had begun to ebb. The entire residue, after evaporation of the water, amounted to only 8·5 grains. The determination of the constituents, occurring in small quantities, could not therefore afford accurate results. The small amount of chloride of silver precipitated was here also accidentally lost.

7—10. Chandon. *Annales des travaux publics*, t. ix., p. 201.

11. Deville. *Loc. cit.*

12. Boussingault, in his *Rural Chemistry*.

13. Dupasquier. *Boussingault's Rural Chemistry*.

14. Tingry. *Ibid.*

15. Deville. *Loc. cit.*

16. Deville. *Ibid.*

17. Deville. *Ibid.*

18. Bouchardat. *Boussingault's Rural Chemistry*.

19. Bennett. *Quart. Journ. Chem. Soc.*, vol. ii., p. 199. From the quantities of chlorides of calcium and magnesium and sulphate of soda given as constituents, the corresponding quantities of chloride of sodium, sulphates of lime and magnesia, have been calculated, since they cannot exist together in aqueous solution.

20. Clark. *Ibid.*, vol. ii. p. 76. The same correction, with regard to sulphates and chlorides, was applied to this analysis as to the former.

21. Ashley. *Ibid.*, vol. i., p. 158. The water was taken half an hour after the highest water level had been reached. This analysis is certainly incorrect. When from the quantities of chloride of calcium and sulphate of soda the corresponding quantities of chloride of sodium and sulphate of lime were calculated, there still remained the unusually large quantity of 6·24 chloride of calcium, which salt is not indicated by either of the previous or by the following analyses. Moreover, in the direct determination of the solid constituents, which gave 40·06, there is a considerable discrepancy.

22—27. Graham, Miller, and Hofmann. Report by the Government Commission, on the chemical quality of the supply of water to the metropolis. London, 1851.

These nine analyses of the water of the Thames give greater quantities of chloride of sodium than are contained in other rivers; there can, therefore, be no doubt that this salt proceeds from the intermingling of the sea water with water of the river by the tide. The sulphate of lime also is very predominant; a portion of it may, therefore, have the same origin. At the same time it is remarkable that No. 19 only gives sulphate of magnesia, and that chloride of magnesium is not given in any of the analyses; perhaps, seeing that in Nos. 22—27 sulphates of the alkalies make their appearance as constituents, the magnesian salts may have been decomposed by the carbonates of the alkalies which pass into the Thames from chemical manufactories in London and its vicinity.

It is remarkable that the analyses 22—27 give 8·25 to 11·83 parts of free carbonic acid in 100,000 parts of water. It may be seen from this, that still



greater quantities of carbonate of lime than were found might have been dissolved.

28. Th. S. Herapath. *Chem. Gazette*, 1848, p. 429.—The large proportion of chloride of sodium and sulphate of lime, and the small quantity of carbonate of lime, show clearly that this river water was mixed with a large quantity of sea water.

29. John Smith. *Chem. Gazette*, 1851, p. 157. The sources of the Dee are in the midst of granite mountains. The water was taken three days after a heavy rain.

30. John Smith. *Ibid.* The Don flows over granite, but more frequently than the Dee over limestone. The water was taken about 1 mile above the mouth of the river. A sample collected at a higher point contained less mineral matter.

31. Pagenstecher. *Loc. cit.* The Lüttschine issues from the lower glacier of Grindelwald, and enters the Aar.

32. Schlagintweit, Herman, and Adolph. *Untersuchungen über die physikal. Geographie der Alpen*, 1854, p. 298. The Möll issues from the Partern glacier, and enters the Drau near Möllbruck.

33. Schlagintweit. *Ibid.* The Oetz, a considerable glacier river, flows from the Hintereis- Hochjoch- and Vernagt glaciers, and enters the Inn 22 miles above Innsbruck.

These two rivers rise in the chain of crystalline slate rocks.

34. Pagenstecher. *Loc. cit.*

35 and 36. Tingry. *Bouss. Rural Chemistry*. The Arve receives all the glacier water of the Chamouni valley.

37. Deville. *Loc. cit.*

38, 39, and 40. Bouchardat. *Bouss. Rural Chemistry*.

41, 42, 43, and 44. Colin. *Ibid.*

45, 46, and 47. Maumené. *Comptes rendus*, t. 31, p. 270. This chemist found that none of the river waters of the region of Rheims contain magnesia.

48. Maumené. *Ibid.*

These four rivers enter the Seine.

As the analyses from 1 to 30 are of rivers which fall directly into the sea, they afford a criterion of the mineral constituents which are thus carried into the sea in a state of solution.

The quantity of dissolved matter in the Maes decreases considerably the greater the distance from Hocht; on the contrary, the quantity of sulphate of lime in the water at Pierre-Bleue amounts to about three times as much as in that at Hocht and Bocholt, which, according to Chandelon, is probably to be ascribed to the proximity of brown coal, or other rocks, containing iron pyrites. He offers no explanation of the great diminution in the quantity of mineral matter.

Hermann and Adolph Schlagintweit\* found the spring of the Drau, near Innichen, 4198 feet above the level of the sea, to contain 68·14 mineral substances in 100,000 parts; and they state that this river deposits calcareous tufa at a short distance below its source. If this mineral matter consisted entirely or chiefly of carbonate of

\* *Loc. cit.*

lime, this deposition might be readily explained, for in that case the water would be nearly saturated with carbonate of lime. The waters of the following rivers, which rise in limestone mountains, are far from being saturated with this substance.

100,000 parts of the water				Carbonate of lime.	
of the	Ammer ....	....	....	43.0	} Schübler.*
"	Neckar	....	....	45.6	
"	Pader ....	....	....	25.3	} Bischof.
"	Lippe ....	....	....	22.6	
"	Alme ....	....	....	18.0	

These analyses lead to the following results:—

1. Among the mineral substances which occur in these rivers carbonate of lime is always in the largest quantity. The Exe only forms an exception: this, however, as was already observed, depends undoubtedly on an admixture of sea water. In the Loire it amounts to 35, in the Thames from 43 to 57, in Lake of Geneva 47, in the Elbe 55, in the Maes from 48 to 62, in the Rhine, at its usual height, from 55 to 75, in the Danube 67, in the Aar and the Seine 75, and in the Rhone, at Lyons, 82 to 94 per cent. of the total mineral matter. The immense limestone mountains, through which most of these rivers flow, account for the large quantities of carbonate of lime. The waters of the Rhine, Maes, Rhone, and Seine show how greatly the proportion of this carbonate varies at different levels of their water.

It is interesting to observe that the substance present in these rivers in the largest quantity is precisely that which we know with certainty to be continually abstracted from sea water by shell-fish. If it is assumed that the mean quantity of carbonate of lime in the Rhine is 9.46, then, according to Hagen's estimation of the quantity of its water flowing at Emmerich, it will be found that the quantity of carbonate of lime annually carried into the sea by this river is sufficient for the formation of the shell of 332,539 millions of oysters of the usual size.

2. The relatively smaller quantity of carbonate of magnesia in rivers corresponds with the usually smaller proportion of this carbonate in limestone. When the river district intersects dolomite or dolomitic limestone, the carbonate of magnesia is present in larger proportions in the river water. Dolomitic limestone occurs in the Bernese Alps, in Bündten, and in the neighbourhood of

\* Kastner's Archiv. Vol. 5, p. 12.

Mont Blanc, and it is on this account that the proportion of carbonate of magnesia in the Aar, the Rhine, and the Arve, is somewhat greater. But even when springs and rivers rise in dolomite itself, the carbonate of lime which they contain must always predominate over the carbonate of magnesia, because, according to my experiments, carbonated water extracts either no carbonate of magnesia at all from dolomitic limestone, or only very feeble traces. I shall again refer to this subject in the chapter on Dolomite.

3. In the rivers falling directly into the sea, the salt, which after carbonate of lime occurs in the largest proportion, is the sulphate of lime. In a few small rivers only, as in 15, 16, 32, 37, 45, to 48, does the salt fail. This substance would be found in rivers in larger quantities than the more difficultly soluble carbonate of lime, if gypsum rocks were not altogether insignificant when compared with limestone rocks. When in the river district, gypsum is abundant, as in those of the Ourcy, the Bièvre, and the Beuvronne, the quantity of sulphate of lime approaches very near to that of the carbonate, and even in some cases exceeds it. The large quantity of sulphate of lime in proportion to carbonate, which is contained in the Arve, originates in the masses of gypsum upon the western side of Mont Blanc and in Chamouni.\* The sulphate of lime predominating in the Rhone, at Geneva, as well as in the Lake of Geneva, originates in the gypsum occurring in the slate of Wallis, up to St. Gothard.† The source of the sulphate of lime in the Lütchine, which is very considerable in proportion to the carbonate, does not appear to have been pointed out geognostically. Ebel,‡ however, found a piece of very fine alabaster upon the edge

\* B. Studer *Geologie der Schweiz*. Vol. 1, p. 411.

† Ibid. The much smaller proportion of sulphate of lime indicated in the analyses of the water of the Rhone at Lyons than in that at Geneva, must be ascribed to an error in the determination; for, since the quantity of this salt in the Rhone is increased by the confluence of the Arve, it cannot be supposed that the former should be so far diluted by the Saone, which discharges into it a much smaller quantity of water, that the proportion of sulphate of lime should be considerably diminished. Moreover, the comparison of the proportions of this salt with those of the sulphate of magnesia indicated in the three analyses of the Rhone and in the water of the Lake of Geneva, shows such differences, that they must be attributed to errors in the determination of these sulphates. If most confidence is to be placed in the analysis No. 11, we must conclude that the relative proportion of the sulphate of lime to the sulphate of magnesia given in it, holds in regard to the water of the Lake of Geneva; also, since the variation in the height of the water in this lake amounts annually to only 5 or 6 feet, and since this variation is insignificant when compared with its depth of 950 feet in some places, the greater or less quantity of mineral matter carried into it by the Rhone would not sensibly alter the absolute quantity of mineral matter in this lake.

‡ *Anleitung die Schweiz zu bereisen*. 2nd edit., Vol. 2, p. 430.

of the large glacier at Grindelwald. At all events, the limestone under this glacier must contain considerable masses of gypsum.\* Sulphate of lime is also present in large quantity in the water of the Aar, near Berne, and is derived from the gypsum situated at the Thunersee, and extending from thence under the chain of the Niesen.† The sulphate of lime in the water of the Rhine is probably not carried into it by the Aar alone, but is derived partly from the gypsum in Graubünden.‡

4. The great quantity of sulphate of magnesia indicated by some of the above analyses, for instance, in the waters of the Aar and the Arve, is remarkable. Even if this depended in part upon an incomplete separation of the lime and magnesia, still the analysis of Rhine water (4), in which I gave especial care to the separation of these earths, shows a quantity of sulphate of magnesia which approaches very near to that of the sulphate of lime. In the Danube, the quantity of the former surpasses even that of the latter. On the other hand, the total absence of sulphate of magnesia in the analyses of the Thames, from No. 22 to 27, the nearly accordant results of which indicate a very careful execution, is very remarkable.

5. The quantity of the chlorides which are carried into the sea by rivers, the Thames and the Exe excepted, whose large proportion of chlorides is evidently derived from sea water, is very small.§ These salts consequently reach the sea and accumulate therein in much smaller quantity than the sulphate of lime and the sulphate of magnesia. The sulphates of the alkalies also, which are carried into the sea on coming in contact with its chloride of magnesium, give rise to the formation of sulphate of magnesia.

6. Although alkaline carbonates are frequently present in springs, especially in mineral springs, these analyses do not indicate their presence in the water of any of the above rivers, except that of the Garonne, in which carbonate of soda was found; the alkaline carbonates carried into the other rivers must, therefore,

\* In the moraines of glaciers the rocks of the highest and frequently inaccessible rocks of the central chain may be studied; but of the rocks under the glaciers there are only crushed fragments, sand and gravel, found in the beds of the glacier streams. Here the chemical analysis of these streams might complete the geognostic investigation. By this means it might be determined whether gypsum and other soluble substances occur in the rocks supporting the glaciers.

† Ebel. Loc. cit. Vol. 3, p. 253.

‡ Studer. Loc. cit.

§ A few small rivers, which are especially rich in chloride of sodium and other chlorides, must be regarded as exceptions to the rule. But these rivers seldom fall directly into the sea.



have partially decomposed the earthy salts, sulphates of lime and magnesia, chlorides of calcium and magnesium.

7. Although the presence of a silicate is indicated only in the analysis of Loire water, silica occurs in all the other waters,\* and there are good reasons for the opinion that silicates are present in all, and are carried into the sea.

8. The quantity of organic substances which reach the sea through the medium of rivers, is by no means inconsiderable, as is shown in particular by the analysis of the water of the Thames. It is, no doubt, by means of these organic matters, along with the remains generated in the sea by the death of marine animals and plants, that the sulphates conveyed into the sea are decomposed and the equilibrium restored.

Since the above-mentioned rivers, together with their tributaries, flow through all kinds of sedimentary and crystalline rocks, it may be assumed, with great probability, that generally speaking, all the other rivers upon the earth carry into the sea nearly the same relative quantities of mineral constituents.

It can scarcely be considered that the mineral substances in river waters were present in the same proportions at the former as at the present time; for the more soluble would be, for the most part, extracted from the rocks first. The chlorides with which the marine sedimentary strata were impregnated, have, therefore, been long since conveyed again into the sea. The less soluble substances, carbonate and sulphate of lime, on the contrary, were certainly always present in river waters, in nearly the same proportion as at the present time, for extensive deposited masses of limestone and gypsum are still in existence.

It has already been remarked, that the mineral substances in river waters are subject to great variations. The above analyses of the Rhine, Rhone, and Seine waters, which were taken at different times, but also at different places, show these variations. The Rhine water 3, which contains scarcely half as much mineral constituents as 2, was taken at the time when the river was much swelled by melted snow. On the other hand, the water 4, taken

\* The analyses by Deville, and my analyses of Rhine water, give the largest quantity of silica. The mean quantity of silica in the former analyses corresponds very closely with the mean quantity found in several springs and well waters also analysed by Deville. It is, therefore, very probable that the much smaller quantity, or even total absence of silica in the other analyses, results merely from an imperfect determination. It is evident that the quantity of silica in river water cannot fall below that in spring waters, except after continuous rain, or the melting of snow.

when the water was low, shows, on being compared with 3, a considerable increase.

The analysis of the water of the Dee (29), shows an uncommonly small quantity of mineral matter, amounting, after deducting the organic substances, to only 3.12. Crystalline rocks, which, like granite, contain no calcareous silicates, can yield to river waters silica, silicates, and carbonates of alkalies, for the most part only by decomposition of feldspar.

The Don water (30) contains, after deducting the organic substances, only 8.07 mineral matter. The larger quantity of carbonate of lime is owing to its coming in contact with more limestone. The proportionally large quantity of chlorides is, perhaps, to be ascribed to the introduction of sea water at high tide, as in Thames water.

The analyses 32 and 33, show how little mineral matter the glacier streams are capable of dissolving, when the rock supporting the glacier is not limestone. It is also natural, that water formed by the melting of glacier ice, and flowing in great quantity beneath the glaciers, cannot dissolve so much mineral matter as spring water, which flows in narrow channels and comes into more intimate contact with rocks. The analysis 31, however, shows how greatly the quantity of mineral matter increases when the glacier streams come in contact with limestone.

The glaciers melt only in summer, and the more, the higher the temperature; for the little water which flows from them in winter, is only spring water. When, therefore, the Alpine streams are swollen by glacier water during the summer, the proportion of mineral matter in them decreases. The analyses of the Arve (35 and 36) show this difference. In February, when this river is fed only by springs, it contains nearly double as much mineral matter as in August, when the spring water is diluted by glacier water. Besides the circumstances already mentioned which tend to cause a variation in the quantity of mineral matter, we find here another which, however, occurs only in the Alpine streams.

The smaller quantity of mineral matter in those Alpine streams which, like the Rhine and Rhone, empty themselves into large lakes, is recognisable only above these lakes.\* In the Lake of Constance, 34 square miles in extent, as well as in the Lake of

\* In these two rivers the annual variations in the quantity of mineral matter above the Lakes of Constance and Geneva must be very considerable, for the Rhone receives, within a distance of 35 leagues in Wallis, the water from 135 glaciers.—*Terrain erratique alluvien du bassin du Léman, &c., par R. Blanchet. Lausanne, 1844, p. 12.*

Geneva, the annual variations in the height of water, resulting from the greater or less influx from the Rhine, and other less important rivers, cause no sensible alteration in the quantity of mineral matter. It may therefore be safely inferred, that the Rhine, flowing out of the Lake of Constance, always contains nearly the same quantity of mineral matter.\* Consequently, an analysis of the water of the lake would give the normal composition of the Rhine water flowing out of it, at whatever time of the year the water was taken. The comparison of these analyses with that of the Rhine, at any spot below Constance, would then decide whether it received more or less mineral matter from its tributaries.

At first sight, the constituents which are carried into the sea in a state of solution, may appear inconsiderable; when, however, the large volume of water which is constantly flowing into the sea, is taken into consideration, this amount must be very great. Rivers like the Rhine, the Danube, the Rhone, and the Elbe, which

\* The mean depth of the Lake of Constance, derived from 88 soundings, is 279 Paris feet. The variation in the height of water in the year 1827 amounted, according to Dihlmann (*Jahrb. der Chemie und Physik*, T. 59, p. 30), to 7·9, in the year 1828 to 5·7 Paris feet. This annual variation is, therefore, equal to 2·0 or 2·8 per cent. of the total volume of water in the lake. Consequently when, during the melting of the glaciers, water flows into the lake containing even only half as much mineral matter as its water, the dilution would be so slight that the difference could scarcely be detected by analysis. The temperature of the Rhine water flowing into the lake in the summer is undoubtedly lower than that of the lake water, for the former is chiefly glacier water. It, therefore, sinks, and the intermixture is favoured by the motion of the waves. According to Dihlmann, the temperature of the lake water rises to 80° F. in July. The Rhine water flowing into the lake would certainly not acquire this temperature. In September, 1833, I found the temperature of the Aar, flowing into the Thuner Sea, to be 4°·5 F. lower than that of the lake water. Escher (*Gilbert's Annal. der Physik*, t. 70, p. 202) calculates, from the observations made by Stehlin from 1809 to 1820, on the height of the Rhine at Basle, that 1046 million cubic toises of water are annually carried away by this stream. This quantity of water would occupy a place in the Lake of Constance 56 feet below the surface. As its mean depth is five times as great, then, presupposing that rivers which fall into the Rhine between the Lake of Constance and Basle, of which the Aar is the most considerable, contain together as much water as the Rhine flowing out of the Lake of Constance, this latter would only be filled in 5 years by the water of the Rhine at Basle, and the water of the Rhine which flows into it in about 10 years. After these remarks, it must be evident that it would be very interesting if Swiss chemists undertook the analysis of the waters of the Alpine lakes. Besides the Lakes of Constance and Geneva analyses of the waters of the Brienzer, Thuner, Vierwaldstadter, Zürcher, Como, and Maggiore lakes would make us acquainted with the substances which are extracted from the Upper Alps by water. If these analyses were connected at the same time with those of the rivers flowing out of these lakes, and falling partly into the sea, and partly into other rivers, we should know what substances are extracted from rocks below these lakes. Although the last-named lakes are much smaller than the Lakes of Constance and Geneva, still it is probable that their constituents are not subject to greater variations than obtain in those lakes; for the Alpine streams flowing through them are much smaller than the Rhine and Rhone.

contain of these constituents at least  $\frac{1}{8000}$ , carry into the sea, in 8000 years, quantities as great as the weight of the water annually conveyed into it by them. But what are 8000 years, compared with geological periods, in which we must reckon millions of years? These periods must be conceived to be of such duration, in order to understand the formation of the extensive sedimentary limestones. But how easy it is to understand, in particular, the formation of these rocks, assuming that the carbonate of lime amounts to 50—94 of the constituents which are conveyed into the sea in a state of solution.

## CHAPTER VI.

### LAKES.

HOWEVER interesting the physical characters of lakes may be (such as their magnitude, depth, temperature, &c.), their chemical characters are not of much importance in a geological point of view. The lakes through which rivers flow, and which are as it were mere local expansions of them, contain the same mineral substances as these rivers. However, the analysis of their waters affords, as has already been remarked, a good opportunity of ascertaining the normal composition of such rivers. There is only one of such lakes, the Lake of Geneva, the composition of whose water is known.\*

Those lakes which receive waters from surrounding heights, but have only subterranean outlets, belong, to a certain extent, to the same class. The composition of their water remains almost constant.†

\* Braconnot (Journ. Chim. Med. (3), Vol. 6., p. 65) found the water of the Lake of Gérardmer, in the Vosges, to be almost free from inorganic substances.

† Such lakes as are situated chiefly in the midst of fissured limestone rocks are abundant. The Zirknitz lake is well known. According to Gruber (Briefe hydrographischen und physikalischen Inhalts aus Krain 1781) and Kröpfer (Ergänzungsband, T. 1, p. 382, to Poggendorff's Annalen), after rain and the melting of the snow, the water rushes out from two large caves into the lake with great force. Besides a number of smaller holes, there are two gorges in particular, of considerable extent and depth, through which the water passes off, forming the Laibach river, which, except at the time when the lake is dried up, is navigable at its immediate source. As this lake is entirely surrounded by mountains, it would not have found a discharge for its water below a height of several hundred feet, had not the fissured rocks afforded it a subterranean passage. The water rushing



In lakes which have supply, but no outlet, and which lose water only by evaporation, the remaining water becomes gradually more charged with mineral substances. The Caspian and Dead Seas, &c., are of this kind. The quantity of water supplied by several hundred of the larger streams flowing into Lake Superior, the largest body of fresh water in the world, is alone many times greater than that discharged at the Falls of St. Mary, the only outlet.\*

Lakes which receive the waters from surrounding heights, even if only periodically, receive also the substances held in suspension. Deposits are formed, the beds of the lakes are raised, and after long periods are entirely filled. The lakes, for instance, through which the Alpine rivers flow, serve to clear their waters. If these lakes are very extensive, they receive, during rainy weather and after the melting of the snow, muddy water, while clear water flows out of them.

Lakes also regulate the flow of rivers. By collecting the water carried down during certain seasons, or after continuous rain, they effect a more uniform flow of the rivers passing through them, and thus prevent inundations. The Lake of Constance rises from the winter until July, and receives about a quarter of the entire quantity of water flowing into it annually. This quantity of water is gradually discharged between July and the next winter. If this lake did not exist, the quantity of water of the Rhine would be much less during the second half of the year than it is now.

Lyell† alludes to the formation of great lakes, and the drainage of others, in the basin of the Red River, in Louisiana, where the

forcibly through the channels renders them considerably wider, and a time will consequently come when the Zirknitz lake will no longer exist. Similar phenomena are presented by the Fuciner lake (Iacus Fucinus of the Romans, *Λίμνη Θουκινά*) in the Apennines, the lake Kopai in Bœtia, lake Phonia in the Morea, and the Dauben lake in Switzerland (p. 71), &c. According to Kramer (*Der Fuciner See*, 1839), the Fibreno river, which issues from a basin several hundred feet in diameter, and is situated immediately at the foot of a steep and lofty precipice, originates probably from this lake. Lake Kopai has also a number of subterranean channels for the discharge of its water, and is almost entirely dried up during the summer (Forchhammer in Poggendorff's *Annalen*, T. 33, p. 241). Several springs originate from this lake after passing a subterranean course of some miles. Their water is slightly saline, owing probably to their coming in contact with beds of salt. According to Boblage (*Annal. des Mines*, T. 4, p. 99), the Lake of Phonia did not exist in 1814, though it has at the present time a depth of from 120 to 150 feet, and a breadth of 18,000 to 24,000 feet. The subterranean channels have since that time been stopped up by the deposition of sand and mud. More than a hundred years ago its surface was above 300 feet higher than that at the present time, as is shown by the deposits of mud at this height. Such stoppage and reopening of its subterranean channels, appear to have been frequent at all times.

\* Lyell's *Principles*, 7th Ed., p. 256.

† *Ibid.*, p. 214.

largest of them, called Bistineau, is more than 30 miles long, and has a medium depth of 15 to 20 feet. In the deepest parts are seen numerous cypress trees, of all sizes, now dead, but yet standing erect under water. These lakes have been formed, according to Darby, by the gradual elevation of the bed of the Red River, in which the alluvial accumulations have been so great as to raise its channel, and cause its waters, during the flood season, to flow up the mouths of many tributaries, and to convert parts of their courses into lakes. It has happened, in several cases, that a raft of timber, or a bar, has been thrown by the Red River across the opening of some of these channels, and then the lakes become, like Bistineau, constant repositories of water.

He also brings forward some instances of the recent origin of large lakes in the basin of the Mississippi, situated 300 miles north-east of lake Bistineau, and formed by the subsidence of land in the years 1811-12.\*

On the other hand, there are some instances of the disappearance of lakes. Thus, since the time of the Romans, extensive lakes and marshes have been gradually filled on the course of the Po, as those near Placentia, Pàrma, and Cremona, and many others have been drained naturally by the deepening of the beds of rivers.†

We have in the table on the next page analyses of the water of the Caspian Sea, the largest of all lakes. The accompanying analyses of the waters of the Black Sea and the Sea of Azoff, show the improbability of a former communication having existed between these lakes.

In the water of the Black Sea, the sulphate of magnesia amounts to 14 times as much as the sulphate of lime; while in the ocean, taking the mean of a great number of analyses agreeing closely, the quantity of the former is only 1·2 times greater than that of the latter. There can be no doubt that the mineral constituents in the water of large rivers falling into inland seas, must exercise a considerable influence upon the constituents of the latter. In regard to this point, it is worthy of notice that the water of the largest stream which flows into the Black Sea, the Danube, contains almost five times more sulphate of magnesia than sulphate of lime.

From single analyses of the waters of the Black Sea and the Danube, however, no safe inferences can be drawn, more particularly seeing that the Danube water analysed was taken in the

\* Lyell's Principles, 7th Ed., p. 215.

† Ibid., p. 205.

neighbourhood of Vienna. But if the water of this river at its mouth, and that of the Black Sea towards its western coast, but at some distance from the mouths of the Danube, were analysed, and particular attention directed to the determination of the sulphate of magnesia and sulphate of lime, it would be seen whether the large proportion of the former salt contained in the above sea is actually derived from the Danube.

	Caspian Sea.		Black Sea.	Sea of Azoff.
	Göbel.*	H. Rose.†	Göbel.‡	Göbel.§
Chloride of sodium ... ..	0·3673	0·0754	1·4020	0·9658
„ of magnesium ... ..	0·0632	—	0·1304	0 0887
„ of potassium ... ..	0·0076	—	0·0189	0·0128
Bromide of magnesium ... ..	trace	—	0·0005	0·0004
Sulphate of lime ... ..	0·0490	0·0406	0·0105	0·0288
„ of magnesia ... ..	0·1239	—	0·1470	0·0764
„ of soda ... ..	—	0·0036	—	—
Bicarbonate of lime ... ..	0·0171	0·0018	0·0359	0·0022
„ of magnesia ... ..	0·0013	0·0440	0·0209	0·0129
Water ... ..	0·6294	0·1654	1·7661	1·1880
	99·3706	99·8346	98·2339	98·8120
	100·0000	100·0000	100·0000	100·0000

In the water of the Sea of Azoff, the chlorides and sulphates bear very nearly the same proportions as in the water of the Black Sea. The smaller per-centage of mineral substances in the

\* Reise in die Steppen des südlichen Russlands. Dorpat, 1838, and Pogg. Annal. Ergänzungsband 1, p. 187. The water was taken 2 werst south-west of the small island of Pischnoi, and 140 werst from the principal mouth of the Ural, from the bottom of the sea, which at this place is 2·5 fathoms deep. The wind was at the time S.S.W., driving the water of the sea towards the shores, and completely preventing any admixture of the water of the Ural river.

† Poggend. Annal. T. 35. p. 183. The water was collected by G. Rose, 75 werst from the four hill islands, the uttermost of those formed by the Wolga at its mouth, and was consequently mixed with Wolga water. Göbel found the influence of this water very decided at a distance of even 300 werst eastwards of the mouth of the Wolga and Achtuba, on the northern shore of the Caspian Sea. As the Analyses of Göbel and H. Rose indicate very nearly equal quantities of sulphate of lime, while on the contrary, the latter gives only one-fifth as much chloride of sodium as the former, it may be inferred that the water of the Wolga contains much sulphate of lime. Moreover, Rose himself remarks that his analyses must be imperfect, because he had only a few ounces of water at his disposal.

‡ Loc. cit. The water was taken in August, almost in the middle of the southern shore of the Crimea, far away from the mouths of rivers, at Feodosia, beyond the quarantine.

§ Loc. cit. The water was taken from the centre of the sea between Kertsh and Mariapol, in July, during fair weather, and from a depth of five and a half fathoms.

water of the Sea of Azoff is easily accounted for by the fact that a very large river, the Don, falls into this sea, which communicates with the Black Sea only through the straits of Jenikale. Then as the ordinary currents flow from the Sea of Azoff into the Black Sea, and in a contrary direction only when there is a strong south wind, much less of the more saturated salt water passes into the former, than of weaker salt water into the latter.

A considerable difference, however, between the waters of the Black Sea and the Sea of Azoff consists in the much smaller quantity of sulphate of magnesia present in the latter, and the much larger quantity of lime in the former.\* One might conclude from this, that the Don carries into the Sea of Azoff much less sulphate of magnesia, and much more sulphate of lime, than are conveyed by the Danube into the Black Sea.†

If the Caspian Sea was ever in communication with the Black Sea, it might indeed be supposed that the waters of both seas had very different compositions, if this communication was effected by a very narrow strait. But in this case, the water of the Caspian Sea would then have been far poorer in mineral substances than at the present time; for as its surface is 86·5 feet below that of the Black Sea,‡ a column of water of this height must have evaporated from the former, since the separation of the two seas, and consequently the per-centage of saline matter, proportionately increased. In addition to this, the large Wolga and numerous other rivers fall into the Caspian Sea, and carry dissolved substances into it, and the delta formations of these rivers have greatly decreased its area.§ Both circumstances would have caused the per-centage of mineral constituents to in-

\* The very small quantity of carbonate of lime in the water of the Sea of Azoff, amounting to only 1·16th of that in the Black Sea, leaves room, however, for the conjecture that the relative quantities of sulphate of lime and sulphate of magnesia have not been determined correctly in the two analyses. In all waters of large rivers hitherto analysed, the carbonate of lime is the predominating constituent. If this, as is highly probable, is the case with the Don also, the water of the Sea of Azoff should, on the contrary, contain more of this carbonate than that of the Black Sea. But every chemist must be aware how easily an error may have crept into the relative determination of the sulphate of lime and carbonate of lime, when both are present in a water in very minute quantities.

† It is to be desired that this, also, might be established by an analysis of the water of the Don, combined, however, with an analysis of the water of the Dnieper.

‡ According to the trigonometrical measurement of Fuss,§ Sawitsch, and Sabler. *Compt. rend.* 1842, T. 15, p. 885.

§ The Caspian Sea is constantly encroached upon and diminished in area by the daily increasing delta formation of the Wolga, the shallow water already extending to forty and fifty miles south of the present embouchure.—R. I. Murchison, De Verneuil, and von Keyserling. *Geology of Russia, &c.* Vol. 1, p. 578.



crease. Since, however, the total per-centage of constituents in the water of the Caspian Sea amounts to only one quarter of that in the water of the Black Sea, it follows that if a communication formerly existed between these seas, this fraction must have been much smaller. But water containing so little mineral matter, is so widely different from that of the Black Sea, that it appears impossible that these seas were ever in communication. We must, therefore, regard Hommaire-Dehel's\* view, that such a communication did exist, as erroneous; and indeed it is inconsistent with his own observations, according to which, more water is removed from the Caspian Sea by evaporation than is carried into it by rivers.

It is remarkable that in the water of the Caspian Sea, also, the sulphate of magnesia greatly predominates, compared with the sulphate of lime, although not so much so as in the Black Sea. It might be inferred from this fact, that the rivers which fall into the Caspian Sea, especially the Wolga, contain, like the Danube, more sulphate of magnesia than sulphate of lime. An analysis of the water of this large stream appears, therefore, desirable.

Murchison† believes that the great saltiness of *some parts* of the Caspian Sea is due to brine-springs issuing from the interior of the earth, often from rocks formed long anterior to the earliest Caspian deposits; for shells, identical with those now living in the Caspian (to the exclusion of nearly every oceanic species), are spread over the lands of vast countries, and have been left at different and considerable altitudes.

Accordingly, the Caspian Sea would appear to have been formerly a great fresh water lake, into which rivers in course of time conveyed the constituents which it now contains in solution. Since among these substances, chloride of sodium amounts to more than all the others together, it is possible that this substance is derived from the numerous salt springs which fall into this lake and its tributary rivers. Whether its former far greater superficial extent is merely the consequence of the decrease of its water by evaporation, or whether, as Murchison‡ supposes, there have been elevations of strata in its neighbourhood, "which were naturally accompanied by adjacent depressions," I will not attempt to determine.

The composition of the water of the Dead Sea is as follows:—

\* Comptes rendus, 1843, No. 15.

† Loc. cit., p. 323 and 308.

‡ Ibid., p. 317 and 324.

	I.	II.	III.	IV.	V.
	C. G. Gmelin.*	R. F. Marchand.†	Th. T. and Herapath.‡	Booth and Muckle.§	Bourton and O. Henry.
Specific gravity ... ..	...	1·185	1·172	1·227	...
Chloride of sodium ... ..	7·078	6·578	12·110	7·855	7·003
" of magnesium ... ..	11·773	10·543	7·822	14·590	5·696
" of calcium ... ..	3·214	2·894	2·455	3·108	0·680
" of potassium ... ..	1·674	1·398	1·217	0·659	0·166
" of manganese ... ..	0·212	...	0·006	...	...
" of iron ... ..	...	...	0·003	...	...
" of aluminium ... ..	0·090	0·018	0·056	...	...
Bromide of magnesium ... ..	0·439	0·251	0·251	...	trace
" of potassium... ..	...	...	...	0·037	...
Muriate of ammonia ... ..	0·008	...	0·006	...	...
Sulphate of lime ... ..	0·053	0·088	0·068	0·070	0·233¶
Silica ... ..	...	0·003	trace	...	...
Nitrogenous substances ... ..	...	...	0·062	...	...
Bituminous " ... ..	...	trace	...	...	Earthy carbonates } 0·953**
Total ... ..	24·541	21·773	24·056	26·319	14·731
Total directly determined ... ..	...	21·671	24·048	...	...
Water ... ..	75·459	78·227	75·944	73·681	85·069
	100·000	100·000	100·000	100·000	100·000

\* Württembergische naturwissenschaftlichen Abhandlungen. Bd. 1, heft. 3, p. 1.

† Poggend. Annal. T. 76, p. 462. This water was taken at the northernmost extremity of the sea, not far from where the Jordan discharges itself into it. Former analyses by Macquer, Lavoisier, and Sage, by Marcet and Tennant, Klaproth, Gay Lussac, Hermbstädt, and Apjohn, differ greatly from each other. The total quantity of substances varies, according to these analyses, between 24·6 and 44·4 per cent. ; a difference which probably arises from the water having been taken in one instance near the mouth of the Jordan, and in others, at a distance from this place. A difference in the substances dissolved in the water may also be caused by the different composition of the sea-bottom, of the strata forming its shores, and containing salt, as the rock-salt mountains of Usdum, on the south.

‡ Quarterly Journ. of the Chemical Soc. Vol. 2, p. 336.

§ Narrative of the U. S. Expedition to the river Jordan and the Dead Sea, by W. T. Lynch. Philadelphia, 1849, p. 509.

|| Journ. de Pharmacie, 1852. T. 21, p. 161. The water was obtained upon the western shore, about 4 English miles from the Jordan. The much smaller proportions of the salts, as compared with those shown by the other analyses, can only be attributable to dilution by the water of the Jordan. As the water of this river, according to the analysis given in Chapter XVIII., contains chloride of sodium in much greater quantity than the other salts, we might in this way account for the relatively greater amount of chloride of sodium in this water.

¶ In addition to sulphate of magnesia, and sulphate of soda, which, however, cannot exist in water in presence of chloride of magnesium.

\*\* As none of the other analyses give carbonates, these must also be ascribed to the Jordan.

The water of this sea is characterised by the extraordinarily large quantity of salt which it contains. The means by which this and several other salt lakes of Central Asia and America may have acquired the large quantity of salt which they contain, will be treated of in Chapter XVIII.

In Hungary, Egypt, and at several places in Asia, Africa, and America, among others, Columbia,\* there are lakes whose waters contain greater or less quantities of carbonate of soda. According to Beudant,† the most considerable of the Hungarian lakes occur in the extensive plains near Debretzin, and the alkaline salt which they yield is collected as an article of commerce. During the summer these lakes dry up, and the efflorescing salt is collected every fourth or fifth day. D'Arcet‡ describes the soda-lakes of Lower Egypt as being situated in the desert, upon the western bank of the Nile, and about twenty miles from it. Their waters contain sesqui-carbonate of soda, chloride of sodium, and sulphate of magnesia (soda). These lakes are fed by a number of small springs, which rise to the eastward, and the lakes themselves are, in fact, merely the basins in which the water of these springs evaporates. De Chancourtois§ describes the Lake Van, situated in Southern Armeristan, near the Persian frontiers, and receiving its waters from the east. It has no outlet. Abich has made known some facts relating to some soda-lakes upon the plain of Araxes.|| They are situated in the immediate neighbourhood of lava-streams. The shore of one of these lakes is covered with crusts of a very hard salt, generally lighter than water, the detached pieces floating upon the surface of the lake like masses of ice. The bottom of this lake is also covered with a crust of salt several inches thick. These lakes are formed by the water of springs which issue from under the lava, forming small bogs, and then collecting together in wide and level hollows, thus presenting a large surface for evaporation.

De Chancourtois and Abich have analysed the water of such lakes; their results are given in the accompanying table, together with those of the analyses of water from the lake of Laach.

\* Palacio Faxan, in the *Journ. of Sc.* Vol. 1, p. 188.

† *Edinb. Philos. Journ.* Vol. 7, p. 259.

‡ *Comptes rendus*, T. 21, p. 579. See also Andréossy, in the *Annal. de Chim.* T. 30, p. 320, and Russegger, in *Karsten's and von Dechen's Archiv.*, T. 16, p. 380.

§ *Comptes rendus.* Vol. 21, p. 1111.

|| *Journ. für Prakt. Chemie.* Vol. 38, p. 4.

	Lake Van.	Lake near Tarschburan.	Lake S.E. of the lesser Ararat.	Lake of Laach.
	De Chancourtois.	Abich.	Abich.	Bischof.
Carbonate of soda ... ..	0·861*	0·98	3·70	0·0113
Chloride of sodium ....	0·938	4·99	21·36	0·0018
Sulphate of soda ....	0·333	0·69	5·57	0·0010
„ of potassa ....	0·055	.....	.....	.....
Carbonate of lime ....	.....	.....	.....	0·0054
„ of magnesia ....	0·055*	.....	.....	0·0021
Silica ....	0·018	.....	.....	0·0003
Peroxide of iron ....	traces	.....	.....	.....
	2·269	6·66	80·63	0·0219
Water ... ..	97·740	93·34	69·37	99·9781
	100·000	100·00	100·00	100·0000

Mineral springs whose waters have a composition similar to that of these lakes, but with a smaller quantity of salt, are very frequent in volcanic districts, especially in the country round the Lake of Laach. The mineral water of Roisdorf, near Bonn, somewhat resembles the water of Lake Van, with the exception that this contains five times as much saline matter. If the water of Roisdorf springs were to collect in water-bearing hollows, forming lakes, it would be partially dissipated by evaporation, giving rise to the formation of soda-lakes, such as those above mentioned. If the evaporation from the lake of Laach amounted to more than its supply of water, a saline substance would ultimately crystallize on it, consisting chiefly of carbonate of soda.

The long-known property of Lough Neagh, in Ireland, of petrifying wood placed in it,† or rather causing its impregnation with iron, induced me to make an analysis of this water. By the kindness of Mr. James Lindsay, of Belfast, I obtained two specimens of water which were taken at two different parts of the lake. Both contained a quantity of greyish brown flocks, which were collected upon a filter. The water of one specimen, which had been placed in a bottle secured by a cork, was, notwithstanding the presence of those flocks, clear and without smell (I.); that of the other specimen was somewhat milky, and had an extremely unpleasant odour, like that of sulphuretted hydrogen (II.),

\* Is stated to exist in solution in the form of sesqui-carbonate.

† Phil. Transact. No. 158, p. 552. I must suppose that farther accounts respecting this remarkable property may be found in other English or Irish works; but I am unacquainted with them.



which was owing to the circumstance that the inner surface of the cork was covered with bladder which had begun to putrify during the transport of the water.

I limited myself merely to the analysis of the insoluble portion of the constituents left on evaporating the water, because the petrificative property of the water can only depend upon these. They were found to be—

				I.	II.
Carbonate of lime	....	....	....	0·00170	0·00189
“ of magnesia	....	....	....	trace	trace
Peroxide of iron	....	....	....	0·00021	0·00026
Alumina	....	....	....	trace	trace
Silicic acid	....	....	....	0·00014	0·00013
				<hr/>	<hr/>
				0·00205	0·00228
				<hr/>	
Soluble constituents....	....	....	....	0·00511	
Suspended matters ....	....	....	....	0·00093	
				<hr/>	
				0·00809	
Water	....	....	....	99·99191	
				<hr/>	
				100·00000	

The soluble constituents consisted, for the most part, of chlorides; they exhibited a distinct alkaline reaction: alkaline carbonates were therefore present, but no alkaline sulphates. On being ignited, they became black and gave off an empyreumatic odour.

From the suspended matter hydrochloric acid extracted iron with minute traces of alumina. Its quantity was too small to admit of being estimated.

In the water of this lake, contrary to what might have been conjectured, there is no great quantity of earthy constituents. It is remarkable rather on account of the extraordinarily small quantities of these. The fact that peroxide of iron is the chief constituent of the suspended matter, is in accordance with the statement in the Philosophical Transactions, that the lapidifying substance is iron, and that when the petrification is only partial, upon burning such a wood, only the petrified part comes to a glow heat, and the ash which is left is attracted by the magnet. It remains to be ascertained whether the suspended parts are introduced into the lake in a state of suspension by the streams which empty into it, or whether they contain in solution proto-carbonate of iron, which, since the water brought into the lake stagnates for a long time, is subsequently oxidized and separated as hydrated peroxide of iron. The small quantity of alumina mixed with it will always be present

in a state of suspension, and might, in the latter case, be precipitated along with the peroxide of iron which separates in the chemical way.

It also remains to be determined whether the petrification of the wood found in the lake is merely incrustation, or whether it penetrates into the interior. In the latter case, the protoxide of iron must naturally penetrate into the interior in the condition of solution, and be deposited there; but then on account of the reducing action of the ligneous matter, not as hydrated peroxide. Mr. Lindsay had the kindness to send me several specimens of petrified wood, which were found on the bank of Lough Neagh, and in the neighbourhood. I have analysed one of these (Chapter XV) but found in it only  $0.54\frac{0}{0}$  of alumina and peroxide of iron, but on the other hand  $97.71\frac{0}{0}$  of silicic acid. It was therefore a silicified wood; and this wood had certainly not been lapidified by the water of the lake. This, as well as the other specimens, resemble so much the silicified wood occurring in the brown coal formations, that there can be no doubt of its having had a similar origin. Lapidified clay is also found in the neighbourhood of Lough Neagh.

## CHAPTER VII.

### THE SEA.

CONSIDERED in a physical point of view, the sea presents phenomena highly deserving of attention. Without, however, referring to these, I shall here consider those only which are of a chemical character.

An extensive series of experiments upon the specific gravity of sea water, in almost every latitude and longitude, and at different depths, has afforded data from which a general inference may be formed, as to the proportion of its saline constituents. I shall omit the older and less accurate determinations, and give only the mean results of more recent and carefully conducted researches.\* They are as follows:—

\* *Physikal. Wörterbuch*. Neue Bearbeitung. T. 6, p. 1619, &c. Muncke reduced the specific gravity to  $32^{\circ}$  F.

						Spec. Grav.
Atlantic, according to Von Horner	...	...	...	...	...	1·02875
Antarctic Ocean	...	...	...	...	...	1·02692
Both Oceans, the Chinese Sea included.						
In the northern hemisphere	...	...	...	...	...	1·02795
In the southern hemisphere	...	...	...	...	...	1·02765
In the northern hemisphere, according to J. Davy					...	1·02801
In the southern	"		"		...	1·02712
Atlantic, Pacific, and German Oceans, according to Von Bibra*	...	...	...	...	...	1·0244 to 1·0287
In southern hemisphere, according to Jackson†	...				...	1·026 to 1·0275
Atlantic, Pacific, Bay of Bengal, and Indian Ocean, according to Darondeau‡	...	...	...	...	...	1·02545 to 1·02577

According to Von Horner, J. Davy, and Von Chamisso, the specific gravity is greater in low than in high latitudes. From the equator to  $45^{\circ}$  N., it is, according to Lenz, equal at all depths. According to Fischer, it steadily diminishes from  $60^{\circ}$  to  $81^{\circ}$  N. The lowest specific gravity of sea-water in these latitudes was, at the surface, 1·0086; while, at a depth of 240 feet, it rose to 1·0275. It is self-evident, that the water taken from between ice, at the surface of the sea, must have a less specific gravity than that in lower latitudes. In  $78^{\circ}$  N. and  $7^{\circ}$  E., Scoresby found it to be 1·0259; the mean specific gravity of all the specimens of water examined by him, from the Greenland Seas, being 1·02809. Inland seas form an exception: in Baffin's Bay, the same author found it only 1·020. As shown by accurate experiments, the specific gravity of the Baltic is only 1·014, that of the Black Sea, according to Göbel,§ 1·01365, while that of the Mediterranean is greater than that of the ocean.

Where large rivers empty themselves into the sea, its specific gravity is diminished. In this way it falls in the German Ocean, according to Mulder,|| to 1·0255; and near George Town, at the mouth of the Demerara, it was found by J. Davy¶ to be only 1·0036; at 80 miles distance, however, it rose pretty regularly as high as 1·0266.

Since the estimates of the specific gravity of the water of the sea begin to vary only at the third decimal, and are dependent

\* The latitudes and longitudes from which the specimens of water were taken are given p. 101.

† Silliman, Amer. Journ. (2) Vol. 41.

‡ Annal. de Chim. et de Phys. 1838, T. 69, p. 100.

§ Ergänzungsband zu Poggendorff's Annal. T. 1, p. 187.

|| Poggendorff's Annal. T. 39, p. 513.

¶ Edin. New Phil. Journal. Vol. 44, p. 43.

upon the temperature, they do not enable us to distinguish the variation in the amount of solid constituents with nearly so much accuracy as their determination by chemical analysis.

The first analyses which furnished any positive knowledge of the chief constituents of sea-water, were those made by A. Vogel.\* Proceeding upon the opinion that the substances contained in sea-water exist in the same combinations as successively separate from it upon evaporation, this chemist maintained correctly, that it contains no chloride of calcium, and no sulphate of soda, and that the only deliquescent salt present is the chloride of magnesium.

It can only be of interest for the geologist to know what salts are deposited during the evaporation of sea-water, and in what order this deposition takes place.

Marcet,† and John Murray,‡ were of opinion that in solutions of acids and bases, the strongest acids are combined with the strongest bases; and therefore, that sulphate of soda, chloride of sodium, chloride of calcium, and chloride of magnesium, form the constituents of sea-water. In a later analysis of sea-water, from the neighbourhood of Portsmouth, Marcet§ found a considerable quantity of carbonate of lime, but no carbonate of magnesia, no chloride of calcium, and no sulphate of soda.

Bonsdorff|| took the trouble to evaporate, during eight months, by means of the air-pump and sulphuric acid, a portion of sea-water from the German Ocean, near Heligoland. In this way he obtained small crystals of gypsum, which amounted to 0·085%: that is, three-eighths of the maximum quantity of sulphate of lime which can be dissolved by water.

In the following tables of analyses of sea-water, the constituents have been arranged throughout according to Vogel's view. Older analyses, which evidently give the relative quantities incorrectly, are omitted.

\* Schweigger's Journ. Vol. 8, p. 351, and Vol. 13, p. 344.

† Gilbert's Ann. Vol. 63, p. 156.

‡ Ibid., p. 203.

§ Annals of Philosophy. 1823, April, p. 261.

|| Poggendorff's Annal. Vol. 40, p. 133.



## GERMAN OCEAN.

	I.	II.	III.	IV.	V.	VI.
Solids in 100 parts of water	3·76	3·19	3·05	3·27	3·15	3·28
Chloride of sodium in 100 parts of solids .... }	80·90	77·94	77·41	78·71	77·78	79·14
Chloride of magnesium ....	8·56	7·59	9·10	8·74	8·12	8·54
Chloride of potassium ....	.....	4·24	3·31	0·25	0·97	2·06
Chloride of calcium ....	.....	.....	.....	.....	1·39	.....
Bromide of magnesium ....	.....	.....	.....	0·09	0·47	.....
Bromide of sodium ....	.....	.....	.....	0·31	.....	.....
Sulphate of lime ....	4·01	3·77	3·65	3·71	3·47	3·39
„ of magnesia ....	6·53	6·46	6·53	7·74	6·79	6·87
Carbonate of lime ....	.....	.....	.....	0·40	0·56	.....
Silicate of soda ....	.....	.....	.....	0·05	0·25	.....
	100·00	100·00	100·00	100·00	100·00	100·00

I. From the open sea, according to Marcet.\*

II. From the English coasts, according to Clemm.† He found, in addition to the ingredients stated in the analysis, small quantities of carbonates of lime, magnesia, and protoxide of iron, phosphate of lime, bromine, iodine (?) silicic acid, and organic substances. Sea-water from Norderney, according to Soltmann, agrees entirely with this analysis.

III. From the coasts of Heligoland, according to Backs.‡

IV. Some miles from the coast of Havre, according to Figuier and Mialhe.§ They found traces of protoxides of iron and manganese also, as well as traces of carbonate and phosphate of magnesia.

V. From the coast at Havre, according to Riegel.||

VI. From the English Channel, between Belgium and England, according to my analysis.¶

In the analyses from II to VI, the amount of solid constituents, as well as the proportions of the more easily determined salts, chloride of sodium, chloride of magnesium, sulphate of lime, and sulphate of magnesia, approximate so closely, that no doubt can be entertained as to the identity in composition of the water of

\* Philos. Transact. 1819, p. 161, and 1822, p. 351.

† Annal. de Chim. Vol. 37, p. 111.

‡ Journal für pract. Chemie. Vol. 34, p. 185.

§ Journ. der Pharmacie. (3) Vol. 13, p. 406.

|| Jahrbuch für Pharmacie. Vol. 22, p. 5.

¶ I have limited my analysis to the chief constituents of sea-water, but determined the potash with particular care.

the German Ocean in different parts of its extent. Even the analysis I, though made at a time when the more recently discovered constituents of sea-water were unknown, approaches the others very closely. The analyses IV and V differ, it is true, very widely from II and III, in regard to the quantity of chloride of potassium; this, however, is no doubt owing to differences in the methods employed. According to my analysis, the amount of this salt in the former is too low, in the latter too high. The chloride of calcium in V, which is not indicated either in the analyses I to IV, or in any other well-conducted analysis of sea-water, is no doubt owing to a different distribution of the chlorine amongst the metals. Since the sulphuric acid, when the analysis is well performed, is always found in such proportion as to take up the entire quantity of lime present, as well as so much of the magnesia as does not go to the formation of chloride of magnesium, the presence of chloride of calcium in sea-water must be regarded as altogether doubtful. Every chemist is aware that the correct allotment of the lime is very difficult, especially when, as in the analyses IV and V, there are small quantities of carbonate of lime present, which cannot be determined in the direct way with accuracy. The chloride of calcium which is carried into the sea by some rivers, is undoubtedly decomposed by the alkaline carbonates which are brought by others.

The analysis (No. VII)\* of water from the German Ocean also approaches very closely, in most respects, to those already given, and consequently indicates, in like manner, the identity of its waters in composition. From the discrepancy, however, in the relative quantities of chloride of sodium and chloride of magnesium, it may be observed in what way differences may arise, which are not founded on any dissimilarity in composition, but partly on a different method of analysis, and partly upon an unlike distribution of the electro-positive and electro-negative constituents.

The following very valuable series of analyses of the waters of the German, Atlantic, and Pacific Oceans (VII to XVI) was communicated by Von Bibra.† The water, where not otherwise stated, was collected at a depth of about twelve feet below the surface. He allotted the sulphuric acid to the potash. For the purpose of enabling a comparison to be made between these analyses and

\* See following table.

† *Annalen der Chemie u. Pharmacie*. T. 77, p. 90. So large a number of analyses, executed by the same chemist and according to the same method, are very valuable; for they afford more points of comparison than analyses accomplished by various chemists and by different methods.

those already given, I have, however, allotted potassium, corresponding to the quantity of potash present, to chlorine, and the sulphuric acid to the magnesia. In this way the quantity of the sulphate of magnesia is increased, while that of the chloride of magnesium is diminished.\* In most of the residues left, upon evaporating the water to dryness, Von Bibra found traces of *phosphoric acid*.

	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.
Solids in 100 parts of water ...	3.44	3.47	3.84	3.28	3.68	3.52	3.47	3.48	3.57	3.26
Chloride of sodium in 100 parts } of solids ...	74.20	76.05	76.89	75.80	77.20	73.47	74.58	75.75	78.14	84.57
Chloride of magnesium ...	11.04	9.00	8.05	8.87	8.09	11.64	10.36	8.84	6.54	1.00
Chloride of potassium ...	3.80	4.00	3.33	3.68	3.72	3.45	3.34	3.26	4.33	...
Bromide of sodium ...	1.09	1.15	1.30	1.23	1.20	0.87	1.15	1.21	1.46	1.00
Sulphate of lime ...	4.72	4.60	4.94	4.54	3.94	4.60	4.67	5.18	4.36	6.28
„ of magnesia ...	5.15	5.20	5.49	5.88	5.85	5.97	5.90	5.76	5.17	1.89
„ of potash ...	...	...	...	...	...	...	...	...	...	5.26
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

VII.	Water of	German Ocean in	....	51° 9' N.	3° 8' E.
VIII.	„	Atlantic	....	20° 54' N.	40° 44' W.
IX.	„	„	....	41° 18' N.	36° 28' W.
X.	„	Harbour of Callao	....	12° 5' S.	77° 14' W.
XI.	„	Algodon Bay	....	22° 6' S.	70° 16' W.
XII.	„	Pacific Ocean, at a depth of			
		420 feet	....	25° 11' S.	93° 24' W.
XIII.	„	„	11 feet	25° 11' S.	93° 24' W.
XIV.	„	Off Cape Horn	....	56° 32' S.	68° 47' W.
XV.	„	Atlantic Ocean	....	0° 47' S.	33° 20' W.
XVI.	„	„	....	23° 45' S.	29° 27' W.

The analyses VII to XV, inclusive, agree so closely with one another as to justify the conclusion that the waters of the entire ocean have an essentially similar composition. The analysis XVI differs altogether from these; this discrepancy, however, can hardly be regarded as due to any real difference in the composition of the water. In it the chloride of magnesium is not present in sufficient amount to admit of our allotting the potash to chlorine. It is only on the supposition of an error having been made in the determination of the chloride of sodium that this analysis can be brought to agree with the others, and whether this has been the case can only be determined by repeating the analysis.

It deserves particular attention that the aggregate quantities of

\* This alteration in the distribution of the electro-negative constituents (sulphuric acid and chlorine) and electro-positive (potassium and magnesium) was made in the analysis IV also.

chloride of sodium and chloride of magnesium agree so closely in the various analyses from VII to XV inclusive, the greatest difference between any of them being only 0·7%. This quantity might, indeed, be regarded as the regular proportion in which these salts occur in the water of the ocean. Even in XVI, notwithstanding the discrepancy already mentioned, the difference in question amounts to only 0·98%.

This accords also with Forchhammer's researches.\* According to him, the saline constituents of the northern portion of the Atlantic is subject to but little variation. In water taken in 1844 and 1845, in 60°, 61°, and 62° N., and between 5° and 23° W., the medium quantity of chlorine was 1·945%, the minimum 1·9412%, the maximum 1·9515%, while the proportion of saline constituents was 3·5591%. According to the analyses of Von Bibra, the medium proportion of chlorine is 1·8695%. In latitude 63° 18' south, and 55° west longitude, at a depth of 100 fathoms, the proportion of chlorine was found, by Jackson,† to be 2·02%, that of the salts 3·509%; and in latitude 17° 54' S., and longitude 112° 53' W., at the depth of 450 fathoms, the per-centage of chlorine was 1·985, that of the saline constituents 3·689. The determinations given by Forchhammer and Jackson agree, therefore, very closely; they are only a little higher than the mean of the analyses of Von Bibra.

In the neighbourhood of all coasts, even those of small islands, the amount of saline constituents undergoes a notable diminution. At Thorshavn, in the Faroe islands, the amount of chlorine is only 1·8885%. In the water of the German Ocean it rises scarcely to 1·9. Between Bergen and the Orkney islands it was 1·8997%, and to the south-west of Egersund it was only 1·8278. In the water of the Kattegat it is still lower. In August, 1844, it was at the point of Schonen 1·1077%, and in the winter of same year 0·6212%. I found in the English Channel, between Belgium and England, nearly 1·8118%.

The diminution in question, which is best observed by determining the quantity of chlorine, inasmuch as this amounts to more than a half of all the constituents, can only depend upon the water which flows from the land into the sea. In the case of small islands, where the quantity of such water is small, it must be borne in mind at the same time, that it is constant, and therefore affects the sea-water. The less the depth of the seas near the coast, the

\* Ofversigt af K. Vet. Acad. Förk, Vol. 2, p. 202.

† Loc. cit. The determinations of Jackson were corrected according to the specific gravities given by him.



more marked will be the dilution which is produced in the way just mentioned.

According to Forchhammer, the proportion of the sulphuric acid is subject to greater variation than that of the chlorine. While the latter varies in the Atlantic only 0.01%, the former varies about 0.015%, the maximum quantity in which it is present being 0.2436%, the minimum 0.2289%. Jackson found a difference in the proportion of sulphuric acid amounting even to 0.114%, the maximum of this acid being 0.243%, and the minimum 0.129%. I found in the English Channel, between Belgium and England, 0.2141%. The proportion of lime varies only about 0.0003%, its maximum quantity being 0.0598%, minimum 0.0595%; the magnesia varies about 0.0093%, its maximum being 0.2209%, minimum 0.2116%.

The circumstance that the proportion of sulphuric acid varies more than that of the chlorine, may depend on the greater quantity of the former than of the latter, which is brought to the sea by rivers, as well as on the fact that the chlorine, being a simple body, cannot be decomposed, whereas the sulphuric acid in the sulphates is very easily decomposed by organic substances, and in consequence, sulphurets of this metal take the place of the sulphates. Should, also, according to the facts stated in Chapter IX, a conversion of the chloride of magnesium into carbonate of magnesia take place under the influence of marine plants, the chlorine would still remain behind, and enter into combination with the calcium in the carbonate of lime. The chloride of calcium formed in this way would, however, be again decomposed by the sulphate of magnesia into sulphate of lime and chloride of magnesium. By means of this process of decomposition, therefore, the quantity of chloride of magnesium in the sea-water would not be diminished, but only that of the sulphate of magnesia. This is a salt, however, which is brought into the sea by rivers in no inconsiderable quantities.

It will be seen in Chapter XX that this decomposition of the sulphates takes place on a large scale in the sea. A. Hayes\* examined a number of copper, bronze, brass, and silver coins, which had lain for a length of time in the sea. The two first-named were covered with a crystalline coating of sulphuret of copper, or of sulphurets of copper and tin. Two silver dollars, which had lain for thirty-five years off the coast of Cumana, at a depth of fifty to eighty feet, in a vessel that had been shipwrecked, and which had partly sunk into the mud, and was partly

\* Sillim. Americ. Journ., March, 1851, p. 241.

covered with a layer of coral, from six to twelve inches thick, were found converted, to the extent of 20 and 13·39%, into a crystalline crust, consisting of sulphurets of copper, silver and (gold?). The chlorides contained in the sea-water were present only as adherent traces. Hayes correctly ascribes the formation of these sulphurets to the deoxidation of sulphates by means of organic substances.

In the same manner as metals may be converted into metallic sulphurets, so also metallic oxides and salts may, in the sea, undoubtedly undergo the same change. When such bodies are carried into the sea by rivers, they will undergo such a transformation, and hence we can understand the origin of metallic sulphurets in sedimentary rocks, as, for example, the sulphurets of copper and silver in the Zechstein, and the sulphuret of lead in variegated sandstone.

Since, in the decompositions above remarked, the lime of the sulphate of lime unites with carbonic acid, it remains in the sea-water. Hence we can explain how the variations in the quantity of sulphuric acid should be 33 times greater than those of the lime.\*

Keeping out of view the very discrepant determinations of the amount of the solid constituents in the North Sea (I to V), in the remaining analyses, this amount comes to vary between 3·26 and 3·84 per cent. According to Darondeau,† the amount of fixed substances in the water of the Atlantic, Pacific, Bay of Bengal, and Indian Ocean, is 3·218 to 3·669 per cent. Adopting this determination, the minimum will be 3·218, the maximum 3·84, and the difference 0·622 per cent., or nearly one-sixth of the maximum

\* The chlorine and sulphuric acid in the sea-water may be determined with great accuracy. For the determination of the former by means of nitrate of silver, it is not necessary to evaporate the water, and hence no loss of chlorine can take place. The partial evaporation of the sea-water, for the purpose of concentrating the sulphates and the precipitation of their sulphuric acid by means of chloride of barium, is also unattended by any loss of that acid. Complete analyses of sea-water require much time and care; an abridgement, therefore, of the method employed is very much to be desired. By means of the many, and in part very carefully conducted analyses of sea-water which have been made, its qualitative and even quantitative composition, so far at least as regards its chief constituents, is so accurately known that further analyses of this kind can accomplish but little. Future researches, so far as geology is concerned, can only be directed to ascertain the similarity or dissimilarity of the sea-water in different regions and at different depths, and for this purpose the quantitative determination of the chlorine and sulphuric acid is tolerably sufficient. This, however, requires so little time and trouble, that were a navigator to bring even a hundred different specimens of water from the most different regions, it would require no long time for any chemist to make the above determination correctly in all of them. All that remains to be desired, then, is that researches of this kind were very much multiplied.

† Loc. cit.

quantity of saline ingredients contained in sea-water. According to Von Bibra's determinations and my own, the solid constituents of the North Sea (VI and VII) also fall within the limits above mentioned.

The variation in the amount of fixed substances is explained by a difference in the extent to which the sea-water is evaporated in different latitudes, by the melting of great masses of ice in the Polar regions, and by the influx of large streams. The difference caused in this way would be still more considerable were it not that an interchange of the waters in different parts is constantly taking place, through the agency of the tides and of various currents, such as the great equinoctial.

The amount of saline constituents of inland seas, when compared with that given in the foregoing analyses, presents much greater variations. There are four such seas, the waters of which have been analysed.\*

## MEDITERRANEAN SEA.

	I.	II.	III.	IV.	V.
Solids in 100 parts of water .. ..	3·69	4·07	2·91	3·43	3·77
Chloride of sodium in 100 parts } of solids ....	68·02	66·81	76·73	76·33	78·14
Chloride of magnesium ... ..	14·23	15·07	8·90	8·82	8·55
Chloride of potassium ... ..	....	0·03	2·36	3·24	1·34
Bromide of sodium ... ..	....	....	....	....	1·48
Sulphate of lime ... ..	0·41	0·37	2·07	2·60	3·60
„ of magnesia ... ..	16·93	17·23	9·44	9·01	6·58
Carbonate of lime ... ..	0·41	0·02	....	....	0·30
„ of magnesia ... ..	....	0·47	....	....	....
Peroxide of iron ... ..	....	....	....	....	0·01
	100·00	100·00	100·00	100·00	100·00

I. Some miles off Marseilles, according to A. Vogel.†

II. According to Laurent.‡

III. From the Lagunes of Venice, according to Calamai.§

\* The analyses of the waters of the Black Sea and the Sea of Azoff have been already given (p. 88). For the purpose, however, of facilitating a comparison between the water of these seas and that of the ocean, we again state the per-centage of their saline constituents.

According to Giraud (*Journ. für pract. Chemie*, Vol. 50, p. 51), the water of the Red Sea contains, in the Gulf of Suez, 4 per cent. of salts, and on the passage as far as Bombay 3·9, while that of the Atlantic off the Canary Islands contains 4·4 per cent. As this, however, exceeds all previous estimates of the solid constituents of that ocean, its accuracy may be doubted.

† Schweigger's *Journ.*, Vol. 8, p. 344.

‡ *Journal der Pharmacie*, Vol. 21, p. 93.

§ *Gazetta Toscana delle Scienze medico-fisiche*. 1847, p. 113.

IV. From the harbour of Livorno, according to the same.

V. In the neighbourhood of Cette, 3000 to 4000 metres from the bank, and one metre below the surface, according to Usiglio.\*

Keeping out of view the analyses I and II, which are evidently incorrect, the other three correspond so closely with those of the waters of the ocean, that no essential difference can be recognised between them. In the lagunes of Venice, the water presents itself in a state of dilution from the streams which empty into these. In IV and V, however, the proportion of saline constituents perfectly agrees with that of the ocean.†

According to Forchhammer,‡ the sea-water which contains the greatest quantity of chlorine, is that of the Mediterranean, in the neighbourhood of Malta. Its solid constituents amount to 3·7177%, being, therefore, almost as much as in V, and more than those of the ocean, as indicated by the analyses of Von Bibra. The proportion of chlorine is 2·0046%, consequently 0·05% greater than the maximum quantity in the water of the Atlantic. The quantity of lime which is present in the water of the Mediterranean was also found by Forchhammer to be greater than that in the water of the Atlantic, the relation being 0·064 : 0·0676. Not so, however, with the magnesia: at Gibraltar it was, for example, 0·2133%; farther in, still lower, at Malta, for example, 0·2074%, and at Corfu, 0·1826%.

Into the Mediterranean, water is constantly streaming from the Black Sea, as well as from the Atlantic Ocean. The Black Sea contains only 1·77% of saline ingredients, and the proportion in the Atlantic is also probably less than that in the Mediterranean. Numerous rivers, and amongst these the important Nile, pour into the Mediterranean a large quantity of fresh water. Since in this way, then, it receives on all sides water poor in saline constituents, and yet contains a proportionably greater amount of these than any other sea, it must be by evaporation that its waters are and will be continually concentrated. The cause of this evaporation, again, is to be sought in the dry winds which blow from the shores of Africa.§

\* Comptes rendus, Vol. 27, p. 429, and Annal. de Chim. et de Phys., Vol. 27, pp. 92 and 172.

† As regards the large amount of the solid constituents of the Mediterranean at great depths, see Chapt. XVIII.

‡ Ofversigt, &c.

§ Of the extent to which such evaporation prevails in warm climates, we have an example in the case of the Dead Sea (Chapt. XVIII).



	I.	II.	III.
Amount of salts ....	1.77	1.19	1.77
Chloride of sodium ....	79.39	81.30	84.70
Chloride of magnesium ....	7.38	7.47	9.73
Chloride of potassium ....	1.07	1.08	—
Bromide of magnesium ....	0.03	0.03	—
Sulphate of lime ....	0.60	2.42	0.13
„        magnesia ....	8.32	6.43	4.96
Bicarbonate of lime ....	2.03	0.18	0.40
„        magnesia ....	1.18	1.09	0.08
	100.00	100.00	100.00

I. Black Sea, according to Göbel.

II. Sea of Azoff, according to the same chemist.

III. Baltic, according to Pfaff.\*

In most points, I and II approach so closely to the composition of the Mediterranean Sea, that the Black Sea and Sea of Azoff may be regarded as a water of the former sea, much diluted by fresh water. The very minute proportion of sulphate of lime in I cannot be accounted for, and the less so seeing that the amount of this salt in II approaches pretty closely to that in the Mediterranean. A repetition of this analysis, together with an analysis of the water of the Don, is much to be desired.

The Baltic may also be regarded as a sea-water diluted by fresh water. If we reflect that the rivers of Poland, Courland, Livonia, Estland, Finland, and Sweden, the Oder and the Neva, all empty themselves into the Baltic, and that this inland sea appears insignificant in relation to the large hydrographical basin of its rivers, the small proportion of its solid constituents is not the least surprising.

It is impossible, on account of its position in higher latitudes, for as much water to be removed from the Baltic by evaporation as is carried into it by rivers. It must indeed appear surprising that the proportion of its fixed constituents agrees with that of those in the Black Sea, which, at the same time, lies in lower latitudes than the Baltic. But in the Baltic there is also, in general, an outward current through the channel called the Cattegat, and this stream corresponds, according to Patton,† to an under-current running in the opposite direction. If, by this means alone, an intermixture of the more diluted water of the Baltic with the more concentrated water of the North Sea takes place, a still greater

\* Schweigger's Journ. Vol. 22, p. 271.

† Edin. Philos. Jour. Vol. 8, p. 245.

quantity of the latter water is carried into the Baltic after a continuance of north-westerly gales, especially during the height of the spring-tides. The Atlantic rises, and pouring a flood of water into the Baltic, commits dreadful devastations on the isles of the Danish Archipelago. This current even acts, though with diminished force, as far eastward as the vicinity of Dantzic.\*

The fact that, notwithstanding so often repeated intermixtures of the water of the North Sea with that of the Baltic, the saline constituent in the latter, which only amounts to about half as much as those in the former, does not increase, is an evident proof that this minute proportion of saline ingredients is purely a result of the introduction of fresh water by the rivers which empty themselves into the Baltic, and the small extent to which evaporation takes place in this inland sea.

All those ingredients which are dissolved out of rocks by water must accumulate in the sea, inasmuch as all waters, with the exception of a few lakes which have no visible outlet, empty themselves into it. In recent times, indeed, several such substances have been discovered, some of which have been named in the preceding pages.

Iodine cannot as yet be demonstrated in sea-water, but there can be no doubt as to its presence, inasmuch as it occurs in all organised beings inhabiting the ocean. The detection and estimation of this substance will only be effected when a method of removing the bromides has been devised, which interfere with the action of the reagents employed for the above purpose. Fluorine was detected by Wilson,† first in the water of the German Ocean, and afterwards in sea-water from several other localities. It has also been found by Forchhammer‡ in the sea-water at Copenhagen. The quantity of fluoride of calcium in this water does not, according to him, exceed half a grain in 100 pounds. In different corals he has also found fluorine. According to him, there are also present in sea-water minute quantities of ammonia, manganese, baryta, or strontia, besides iron and silica; the latter two bodies being present in relatively greater proportions.

Phosphoric acid being present in the bodies of the innumerable living organisms which are generated and again perish in the sea, no doubt can be entertained as to its forming an ingredient of sea-

\* Lyell's *Principles of Geology*, 7th Ed., p. 315. Compare von Hoff *Geschichte der Veränderungen der Erdoberfläche*, Vol. 1, p. 73.

† *Chem. Gazette*, 1849, p. 404.

‡ Jameson's *New Phil. Journ.* 1850, April, p. 345, and *Proceedings of the Royal Society of Edinburgh*. Vol. 2, No. 38, p. 303.

water. It has been detected by Forchhammer in the sea-water of Copenhagen. So also in incrustations taken from the boilers of steamboats, Volcker\* has found it present in the proportion of 0·63 to 0·04%.

The large quantities of carbonate of lime which are carried into the sea by rivers, as well as the uninterrupted constancy with which the formation of the shells of testaceous animals goes on, would of themselves lead to the supposition that this substance must be present in sea-water. In several of the foregoing analyses, the proportion is also given in which the carbonates of lime and magnesia occurred in the specimens of water examined. According to J. Davy,† however, it is chiefly in the sea-water near the coasts that carbonate of lime occurs, being present only in very small quantity in water widely distant from land. Sea-water from Carlisle Bay, in the island of Barbadoes, contains in 10,000 parts about one part of carbonate of lime; that in the neighbourhood of the volcanic island of Fayal scarcely a trace; while in the open sea, between the West Indies and Europe, Davy invariably failed to detect it. According to Forchhammer, all sea-water is, after being filtered, found to contain carbonate and phosphate of lime in solution. On examining the deeper portions of the sea-water near the shores, he found that they were richer in lime and poorer in magnesia where the sea-bottom consisted of aluminous marl, containing, at the same time, silicate of alumina and carbonate of lime. He supposes that a portion of the carbonate of lime takes the place of the magnesia contained in the sulphate of magnesia, and that a double silicate of alumina and magnesia is then formed. In this way sulphate of lime must be formed, while carbonic acid is at the same time set free. It deserves to be tried how far this explanation can be confirmed by chemical analysis. When the sea-bottom consists entirely of shells, chalk, or sand, the proportion of magnesia remains unchanged. In 10,000 parts of water from the sea between England and Belgium, I found 0·57 of carbonate of lime, and 0·165 of carbonate of magnesia.

Silicic acid was found by Forchhammer in all the specimens of sea-water examined by him; the greatest amount in which it was present being 0·3 in 10,000 parts of water.

Malaguti, Durocher, and Sarzeaud‡ found a minute quantity of silver in sea-salt, rock-salt, and even in the sea-water in the channel

\* Chem. Gaz. 1850, p. 346.

† Edin. New Phil. Journ. Vol. 47, p. 320.

‡ Annal. de Chim. et de Physique, 3me. Série, Vol. 28, p. 129.

at St. Malo (about 1 milligramme in 100 litres). In different fuci they found it present in larger quantity: in *F. Serratus* it amounted to 0·00001, in *F. Ceramides* to 0·00000001. Lead and copper were also found by them in the ashes of several of these plants—the former in the proportion of 0·000018—but not in sea-water. These metals, according to them, exist in combination with chlorine. Arsenic also occurs in sea-water, as is shown by its having been found in the proportion of 0·000001\* in incrustations taken from the boiler of a steamboat which had been supplied with water from the sea. Daubree states, that in 1 kilogramme of the residue left upon evaporating sea-water to dryness, he found 0·009 gramme of arsenic.

The origin of the large amount of saline ingredients contained in sea-water has long been an object of attention. More than a century ago, Halley† endeavoured to show that it is due to the water which the sea receives from rivers being always more or less impregnated with salts, while in that which it loses by evaporation there are none of these present. In the German edition of my “Geology” I also adopted this view. At that time only two analyses of river water existed; there was consequently no sufficient data from which the amount of salts which are conveyed into the sea by rivers could be estimated. Misled by the large amount of chloride of sodium contained in mineral springs, I over estimated the proportion in which it exists in rivers. Sulphates are carried into the sea by rivers in much greater quantities than chlorides (p. 82). Although it seems that the latter also suffer a decomposition, this merely consists in a displacement of one metal by another, the chlorine always remaining in the sea-water. Whether sulphates are conveyed to the sea in the same quantities as they are decomposed, cannot be determined.

From the salts contained in stratified formations we cannot derive any explanation as to the salts contained in the water of the sea, inasmuch as the former have merely been deposited from the sea. It is then only from the unstratified crystalline rock, such as granite, porphyry, syenite, trachyte, basalt, &c., that the saline contents of the sea could have been derived, inasmuch as these rocks, according to the notions of geologists, have arisen from the interior of our earth. The rocks in question, however, are, as regards their distribution, very subordinate, compared with the others. If, therefore, these rocks have furnished the saline con-

\* Comptes rendus, Vol. 32, p. 827.

† Philos. Transact. No. 344.



stituents present in sea-water, they must have been very rich in such ingredients.

Throughout the whole sedimentary period, from the transition rocks to the tertiary formations, rock-salt has been deposited, although not certainly everywhere. Since it can only be supposed that such deposition took place from the sea, immense quantities of rock-salt must have been withdrawn from it in this way. The layers of rock-salt with which we are acquainted, afford no standard by which an estimation can be made of the amount of chloride of sodium contained in sedimentary formations; for every year new layers are penetrated, and it is quite impossible to conceive the number which may in this way be yet disclosed.

From beds consisting of pure rock-salt, we shall see, in Chapter XVIII, that only very little is carried back to the sea by rivers. The chloride of sodium which is conveyed to the sea, can, therefore, only be derived from that which is contained, in small quantity, in rocks, and which is dissolved out by the water percolating through them. It is impossible, however, that this can be an equivalent for the important beds of rock-salt which have separated from the sea throughout the whole sedimentary period. During this period, therefore, the quantity of chloride of sodium in the sea cannot have increased, but must have decreased, in the same proportion as its deposition in the form of rock-salt, inaccessible to the percolating water, exceeds the quantity derived from crystalline rocks.

The saline constituents of the sea must have existed in it at a period as far back, at least, as the time when the formation of the transition rocks took place. The consideration of conditions and relations, indicating that they must have existed before that time, is foreign to the objects of this work.

Were the sedimentary rocks, which cover the beds of pure rock-salt, once removed by water, and in this manner a way of access opened up for the water to reach the beds, their chloride of sodium would then be again carried into the sea. In order, however, that this should take place, the beds must occupy a position above the level of the sea. Such as are situated below this level, as, for example, the beds at Artern, Stassfurth, and Schöningen, which have been bored to the depth of 562, 576, and 1350 feet below the level of the sea, would be dissolved, indeed, by waters penetrating into them, but salt lakes would then be formed, from which the water could only be carried into the sea provided their level was raised above that of the sea.

The gypsum which is conveyed to the sea by rivers, is not derived from those strata which consist of gypsum and anhydrite, alternating with rock-salt, inasmuch as these are just as inaccessible to the action of water as the others. It necessarily follows, therefore, that previous to the deposition of these beds, the sea-water was also richer in sulphate of lime than it is at present. About three times the amount of this salt now existing in it, however, is more than it could possibly ever contain.\*

In the formation of deposits of pure rock-salt and gypsum, chloride of sodium and sulphate of lime are almost the only salts which were removed from the sea, analysis of the former showing that it contains but very small quantities of chloride of magnesium, sometimes none (Chapter XVIII). With the exception of that found in three localities, rock-salt also contains no sulphate of magnesia. Both these salts of magnesia must, therefore, for the most part, have remained in the sea-water after the deposition of pure rock-salt took place. Since the chloride of magnesium is not unfrequently found in rivers,\* it must also be contained in rocks. In sedimentary rocks which have been formed by depositions from sea-water, the sea is the only source from which it could have been derived.

I have already drawn attention to the large amount of sulphate of magnesia which exists in several rivers (p. 82). It must, consequently, be present in rocks in still greater quantity than the corresponding chloride, and whatever sulphate of magnesia is extracted from sedimentary rocks of sea formation must also be regarded as proceeding only from the sea.

If, consequently, these salts of magnesia must have undergone a relative increase in quantity in seas from which rock-salt and gypsum had been deposited, their presence, on the other hand, in impure rock-salt, which generally overlies the pure, and in sedimentary rocks shows that they were in part withdrawn from the sea-water during the later depositions of limestone, sandstone, and slate rocks. These salts of magnesia, therefore, have been and will again be conveyed to the sea.

Moreover they constitute that part of the ingredients of river water which, along with sulphate of lime, are constantly decomposed by the alkaline carbonates dissolved out of rocks by the

\* If it were not so difficult to determine whether the small quantities of magnesia found in analysing river water be combined with hydrochloric, with sulphuric or with carbonic acid, the chloride of magnesium would be probably detected as a common constituent of this water.

water of springs. In this way are formed chlorides of sodium and of potassium, alkaline sulphates, and earthy carbonates. While the magnesian salts are thus steadily diminishing, the alkaline salts are, on the other hand, constantly increasing, and in this way the original proportions of the ingredients of sea-water to one another are partially restored.

The relative quantities of these ingredients being tolerably constant, an approximate calculation might be made of the quantity of salts at present contained in the sea, especially of those which predominate, were its mean depth known. All attempts, however, to ascertain this have as yet failed.

From the foregoing considerations it follows that the solid constituents of sea-water have, since the Creation, undergone a constant circulation, which still continues and always will continue. We can, however, come to no other conclusion than that the fixed constituents, which are at present held in solution by sea-water, were always present, although perhaps in different proportions.

The proportion of gaseous substances contained in sea-water is important in a geological point of view. The quantity of free carbonic acid in the water of certain seas has been determined. For example, in 10,000 parts, by weight, of water there are contained in the—

Mediterranean	....	1·1	by weight, of carbonic acid, according to Vogel			
Atlantic	....	2·3	"	"	"	"
English Channel	....	2·3	"	"	"	"
The same	....	0·77	"	"	"	Bischof

On the coast of Algiers, Aimé\* examined the proportion of air contained in the sea-water at different depths, and found that either none or only exceedingly small quantities were evolved by it. Water from the depth of 65 metres yielded from 0·01 to 0·02 of its own volume of air; from the depth of 1249 and 1606 metres, it yielded no air, or only a few small bubbles. According to A. Hayes,† the sea-water contains at its surface more oxygen than at a depth of 100 to 200 feet.

During the voyage of the Bonité,‡ portions of sea-water were collected in several places at different depths. The circumstance, however, that the specimens of water which were taken from a considerable depth held in suspension a more or less considerable number of whitish flakes, appears to have exerted an injurious influence on the relative quantities of oxygen and carbonic acid.

\* Poggendorff's Annal. T. 60, p. 404.

† Loc. cit.

‡ Comptes rendus. T. 6, p. 616.

It is probable that in the interval that elapsed between the collection of these specimens and their examination in the College of France, a decomposition of the flakes, as well as of transparent animalcules, at the expense of the oxygen absorbed by the water, took place, and in this way gave rise to a portion of the carbonic acid which was found. The specimens of water collected at the surface were perfectly clear, and hence we may suppose that in these less oxygen was taken up for the formation of carbonic acid.

The results of these researches are given below. In the last column the sum of the oxygen and carbonic acid has been given. This is always the same as the quantity in which these two gases were originally present, inasmuch as the formation of carbonic acid at the expense of the oxygen does not give rise to an alteration in the volume.

TIME AND PLACE.	Depth in Paris feet.	Gas in 100 volumes of water.*	Gases.			Sum of oxygen and carbonic acid.
			Oxygen.	Carbonic acid.	Nitrogen.	
1836, August 30, South Sea, 11° 8' N., } 108° 50' W. ....	0 349	2·09 2·23	0·13 0·23	0·22† 0·40	1·74 1·58	0·35 0·63
1837, March 19, Bay of Bengal, 11° 43' } N., 87° 18' E. ....	0 997	1·98 3·04	0·11 0·10	0·28 1·77	1·59 1·17	0·39 0·87
1837, May 10, Bay of Bengal, 18° N., } 85° 32' E. ... ..	0 1495	1·91 2·43	0·12 0·14	0·25 0·73	1·54 1·56	0·37 0·87
1837, July 31, Indian Ocean, 24° 5' S., } 52° E. ....	0 2243	1·85 2·75	0·18 0·27	0·23 0·96	1·44 1·52	0·41 1·23
1837, August 24, Atlantic Ocean, 30° 40' } S., 11° 47' E. ....	‡ 1994	2·04	0·08	0·59	1·37	0·67

It appears from this table, that the quantity of air increases in proportion to the depth: this is especially the case as regards the carbonic acid. Although the circumstance mentioned renders the relative proportions of the oxygen and carbonic acid some-

\* At 760 mm. barometer, 32° Fahr.

† This quantity of carbonic acid is not certain.

‡ The water which was taken from the surface in this place, was lost.



what uncertain, yet the sum of these exhibits a very considerable increase.\*

On a voyage from Havre to Copenhagen, Lewy† found that the atmospheric air above the sea presented greater variations in regard to its composition than that over the Continent. This stands in connection with the different proportions in which different gases are absorbed by sea-water. Morren, sen.,‡ showed that the air in sea-water, in the region of St. Malo, varied between 1-30th and 1-20th, while that in fresh water varied between 1-45th and 1-30th of the volume of the water. Fresh water loses the air which it contains more easily than sea-water. In ordinary circumstances, fresh water contains, during cloudy weather, 32% of oxygen, and from 2 to 4% of carbonic acid, sea-water 33% of oxygen and 9 to 10% of carbonic acid. After several days of clear weather, the oxygen of sea-water increases, and may reach to 39%, whilst in very cloudy days it will sink to 31%. The more the oxygen increases, the more the carbonic acid diminishes, in consequence of its being decomposed under the influence of the sun's rays, by plants and small animals. When the oxygen in sea-water is evolved in larger quantity than usual, it gives rise to an increase in the proportion of that contained in the atmosphere over the surface of the sea: this is especially the case with those portions of the sea which are more or less surrounded by land, and which exhibit an abundant vegetation. Moreover, it is stated by Lewy, that the amount of oxygen in sea-water is somewhat greater during the day than it is at night, the reverse being the case as regards the carbonic acid; and that simultaneously with the decomposition of carbonic acid by plants, the organic substances contained in sea-water decompose its sulphates, sulphuretted hydrogen,§ and hydro-sulphuret of ammonia, which are always distinctly present in the sea, being produced. These facts, therefore, indicate a very intimate connection between the development

\* When the carbonic acid in the preceding table is taken by weight instead of by volume, it amounts to much less than that found by Vogel and myself: its minimum quantity by weight in 10,000 parts of water is only 0.045; its maximum, 0.35; consequently scarcely half so great as that indicated by my analysis. We cannot attribute this to the circumstance that the specimens procured during the voyage of the "Bonité" were collected either within or very near the Torrid Zone; the difference in absorptive capacity between the warmer waters of the tropics and waters in the channel of colder regions not being so great as to account for the difference.

† *Annal. de Chim. et de Phys.* 1844, T. 8, p. 425.

‡ *Ibid.* T. 12, p. 5.

§ With regard to the presence of sulphuretted hydrogen in sea-water, see Chapter XVI.

of green plants, and the variation in the proportion of gases contained in sea-water. It has been already pointed out by A. and Ch. Morren,\* that green animalcules produce, under the influence of the sun's rays, similar effects upon the gases contained in fresh water.†

The presence of carbonic acid in sea-water is sufficiently proved by the preceding observations, and indeed it might well be asked, how it could possibly be wanting in a fluid in which a far greater number of animals breathe than upon land. In reference to geology it is of particular importance. The carbonic acid contained in sea-water will constantly dissolve carbonate of lime when present upon the sea-bottom. If, as appears to follow from my researches, the carbonate of lime and carbonate of magnesia are present in sea-water as sesqui carbonates, the quantities of these carbonates which I have found in it require 0.165 carbonic acid in order to be dissolved, consequently about one-fifth of the quantity of this acid is present in sea-water. The latter is, therefore, capable of dissolving five times as much of the earthy carbonates as there are actually dissolved. That the sea-water is so far below its point of saturation, as regards carbonate of lime, can only depend upon the constant separation of this carbonate by testaceous animals. By this separation, however, the carbonic acid which had dissolved this carbonate, always returns again into the sea-water. In the sea, therefore, the solution of carbonates, and their separation by organic agency, go on continually, no addition of carbonic acid from without being required.

When limestone rocks are situated at the bottom of the sea, the sea-water constantly dissolves the carbonate of lime, but does not become saturated. Thus, the sea between England and France occupies the basin of a chalk-rock; and we observe, that the separation of the carbonate of lime, by organic agency, keeps the proportion of that salt present in the sea-water far below the point of saturation. Still, it must not be overlooked, that the constant currents in the sea convey the water which has become loaded with carbonate of lime, to remote regions, where either no limestone or only very small masses, present themselves for solution. It is for this same reason, that the formation of new strata of limestone is not always to be looked for where limestone rocks, situated at the bottom of the sea, have been gradually dissolved.

\* Mém. de l'Acad. de Bruxelles, 1841.

† Annuaire des Eaux de la France, pour 1851, par Deville, p. 40. Similar researches were made by Aimé upon algae in sea-water.—Annal. de Chim. et de Phys. T. 2, p. 535.

During the daily evaporation of sea-water, the portions of water which are so removed carry along with them the carbonic acid which they contained. But this cannot give rise to a precipitation of the carbonate of lime, for the quantity of free carbonic acid in the water which is left, being, as we have seen, five times greater than is required to hold the carbonate in solution, even if a temporary precipitation were to take place, the carbonate would almost immediately be redissolved by the free carbonic acid. Moreover, the carbonic acid which has been removed with the vapour of water, is always brought back again by rivers and meteoric waters. The proportion of this acid, therefore, existing in a pure state in sea-water, is subject to but very trifling variations.

All that has been said in reference to carbonate of lime, likewise holds good in regard to the carbonate of magnesia, and the more so, since this salt always separates later than carbonate of lime, even from fluids which have undergone a very high degree of evaporation. Consequently, it is only through organic agency that this salt can be removed from the waters of the sea, as is shown by its presence in chalk-stones of animal formation.

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## CHAPTER VIII.

### MECHANICAL DEPOSITS FROM WATER.

THE deposits from water are partly mechanical, partly chemical; the former result from the separation of suspended matter, the latter from the separation of dissolved matter. I shall consider these two classes of deposits separately, in this and the following chapters. Some sedimentary deposits are both mechanical and chemical at the same time; for instance, when a mechanical deposit is cemented together by a substance deposited chemically. In those mechanical sediments which harden into solid stony masses, the cementing matter is frequently a chemical deposit, although this can be determined by analysis only when the cementing matter is soluble in acids, as for instance, carbonate of lime. Conglomerates are for the most part to be regarded as deposits which have been formed both by mechanical and chemical action.

The formation of mechanical deposits in the sea, from rivers,

can commence only from the coasts. They may, however, extend very far into the sea, as is shown by the great distances to which the currents of some large rivers may be traced. The suspended matter of these rivers will be carried out into the sea as far as their currents extend, and there deposited, or carried still further by ocean currents and winds.\* The chemical deposits, on the contrary, may be formed in the middle of the ocean, as is shown by the coral islands.

Since spring waters are generally speaking clear, or if sometimes turbid, are rendered so only by accidental circumstances, they very rarely form mechanical deposits.

We must distinguish between mechanical deposits formed in the beds of rivers themselves, or in their neighbourhood when overflowed, and those which are formed in lakes through which rivers flow, or in the sea into which these rivers fall.

The further we descend a river towards its mouth, the finer becomes the texture of the sediment. The finest particles alone are carried into the sea. The particles carried away by rivers are generally angular at first, and therefore present great obstacles to transportation. But when the velocity of a river is sufficient to produce attrition of the particles which it has either torn up, collected by undermining its banks, or which have fallen into it, they gradually become more easy of transport. Since the inclination of a river-bed varies materially, it may be able to carry detritus to one situation, but may be unable to transport it further, under ordinary circumstances, in consequence of diminished velocity. But the velocity may be, and often is, so much increased further down, that its original transporting power may be, in great measure, restored. It can now, however, only carry forward such detritus as it may receive or tear up in its course, and the pebbles which were left behind at the place of its first diminution of velocity can only be brought within its power by floods. Rivers whose courses are short and rapid, bear down pebbles into the seas near them, as is the case in the Maritime Alps, &c.; but

\* By numerous soundings made in Lake Superior, it was ascertained that the bottom consists generally of a very adhesive clay, containing shells of the species at present existing in the lake. When exposed to the air, this clay immediately becomes indurated in so great a degree as to require a smart blow to break it. It effervesces slightly with acids, and is of different colours in different parts of the lake.—Lyell's Principles, 7th ed. p. 256. Since the surface of this lake is nearly as large as the whole of England, it is ascertained that earthy matter carried by rivers extends to considerable distances from the shores. There are also currents in this lake in various directions, caused by the continued prevalence of strong winds, and to their influence we may attribute the diffusion of finer mud far and wide over great areas.



when their courses are long, and their velocity lessened, they deposit the pebbles in places where the force of the stream diminishes, and they finally transport more sand or mud to their mouths, as is the case with the Rhine, the Rhone, the Po, the Danube, the Ganges, &c.\*

The water which issues from glaciers is always charged with a considerable portion of mud, produced by the pulverization of the fragments of rock which the glaciers grind down in their ceaseless progress. Thus, water taken from the surface of the Aar, at some metres from the glacier of the same name, contained, according to the experiments of Dollfus, 14·2 parts of impalpable powder in 100,000 parts of water. It is the same with the torrents which issue from glaciers. All of them roll along in a turbid, grey, milky, or dark stream, according to the nature of the pulverized rock.† Martins states, in opposition to Ebel and Durocher, that the waters which flow from glaciers never appear to be of a whitish blue colour.‡ But the colour of the water of glaciers in a state of repose, where it is accumulated in great masses in the lakes of Switzerland, is of a beautiful azure blue, or of a very deep pistachio-green. Thus, the Lake of Geneva, which is fed principally by the waters of the Rhone, which come from all the glaciers of the Valais, is of the former colour; and the Lake of Brienz, which receives the waters of glaciers exclusively, is of the latter colour; but the Lake of Thun, receiving its waters from the Lake of Brienz, with which it communicates across the isthmus of Interlaken, is of a blue colour. Finally, the colour of glacier water when it escapes in the form of rivers, from the lakes, is, like that of the Rhone issuing from the Lake of Geneva, azure blue. This river forms a striking contrast

\* A Geological Manual, by H. de la Beche, 1831, p. 46. By means of artificial embankments, the velocity of rivers is increased, and they are enabled to convey a much larger portion of foreign matter to the sea. Thus the Po, the Adige, and almost all their tributaries, are confined between high artificial banks; and consequently, the deltas of these rivers have gained far more rapidly on the Adriatic since the practice of embankment became almost universal.—Lyell, loc. cit. p. 206.

† Ch. Martins, in *Edinb. New Phil. Journ.* July 1847, p. 86. It is still to be ascertained whether the torrents which flow from glaciers resting upon limestone rocks contain particles of carbonate of lime in suspension, or whether the carbonic acid in these waters is sufficient to dissolve them. In the former case, they would probably be dissolved during the further progress of the stream by the atmospheric carbonic acid absorbed by the water, which would gradually become clear. The Lüttschine, which issues from the Lower Grindelwald glacier, which undoubtedly rests upon limestone, is whitish grey. It would be sufficient to test this water with an acid, to ascertain whether the muddiness was owing to carbonate of lime, or whether particles of other rocks were mixed with it.

‡ I have made the same observation.

with the grey and muddy waves of the Arve, which comes directly from the glaciers of Chamouni, and passes through no lake. But the Rhone is also grey like the Arve, when it enters the Lake of Geneva. I have observed a similar contrast between the colour of the Rhine when it enters the Lake of Constance; and when it issues from this lake. The colour in the latter case is, however, more dark green than blue.

It results from all these facts, that the waters of the Alps are green or blue only when they are free from suspended matter. If this has not been entirely deposited, the water appears green, but if it has been entirely separated the blue colour then appears. The difference of colour in the Lake of Brienz and the Lake of Thun shows this clearly. But the deposition of suspended matter does not take place until the glacier streams empty themselves into the lakes. It is therefore here or in the rivers issuing from them that the blue colour first becomes visible. If these lakes did not exist, the Alpine streams would be just as turbid as any others.

The quantity of suspended matter in rivers is naturally very different at different times and at different depths. Generally speaking, it increases with the height of the water. But differences occur, since the height of water in the main stream does not always correspond with the height of water in its tributaries, and the greatest quantity of suspended matter is carried into it during the first days of rain. In consequence of the decreased velocity of rivers near the bottom, the transporting power is less there than at the surface. On the other hand, the matter held in suspension has there a greater weight.

Since, as has been shown at p. 75, the substances dissolved in river waters are less in quantity the higher the water is, these substances are nearly in an inverse proportion to the suspended matter, as we shall see further on.

Much trouble has been taken to determine the quantity of suspended matter which is annually carried into the sea by a river.\* If this be attempted by evaporating a certain quantity of water, the residue consists both of the suspended and of the dissolved matter, and consequently does not determine the former. A single experiment does not admit of an inference being drawn as to the total quantity annually carried into the sea. To obtain a trustworthy result, these experiments must be continued for an entire year. We are indebted to Everest† for the first investigation of

\* Gehler's *Physikal. Wörterbuch*. Neue Bearbeitung. Bd. 8, p. 213.

† *Journ. of Asiatic Soc. Calcutta*, 1832, March; and *Bibl. Univ.* 1834, p. 47.

this kind. He found that the water of the Ganges contained in 100,000 parts\*

From March 15th to June 15th	....	21·71
„ June 15th to October 15th	....	194·30
„ October 15th to March 15th	....	44·86
Mean	....	86·86

If the minimum quantity be compared with that of the Maes and Rhine, which is stated below, there can be no doubt that he made the determination by evaporating the water. This gives a total annual discharge of 6,368,077,440 cubic feet of mineral matter held in suspension and solution. This quantity would form annually a bed of 79,800 feet length and breadth, and 1 foot thick, or 172 square miles 1 foot thick. In addition to this, it is probable that the Brahmapootra conveys annually as much solid matter to the sea as the Ganges.†

According to Dr. Riddell,‡ the mean annual quantity of solid matter in the water of the Mississippi amounts to 80·32 in 100,000. Further experiments have given only 58·82. It is probable that these results were also obtained by evaporating the water. From the former estimate, Lyell calculates the quantity of solid matter annually brought down by this river at 3,702,758,400 cubic feet, and for the formation of its delta, 13,600 square statute miles in area, 67,000 years.

Barrow, in his Journal, cited by Sir G. Staunton,§ inferred from several observations, that the water of the Yellow River, in China, contained 500 parts of earthy matter in 100,000,|| and he calculated that it brought down in a single hour 2,000,000 cubic feet of earth; so that, if the Yellow Sea be taken to be 120 feet deep, it would require 70 days for the river to convert an English square mile into firm land, and 24,000 years to turn the whole sea into terra firma, assuming it to be 125,000 square miles in area.

According to the daily experiments instituted by Chandellon,¶ the maximum of suspended matter in the Maes, at Liege, during the month of December, 1849, amounted to 47·4, the minimum to 1·4, and the mean to 10.

L. Horner\*\* found in the water of the Rhine, at Bonn, when

\* All the following estimations refer to this weight of water.

† Lyell. Loc. cit. p. 270.

‡ Ibid., p. 218.

§ Ibid., p. 268.

|| Even if this river is always turbid, this is an uncommonly large quantity.

¶ Annales des travaux publics de Belgique. T. 9, p. 204.

\*\* Edinburgh New Phil. Journ. Jan. 1835.

it was unusually low, turbid, and yellow, in August 1833, 31·02 suspended and dissolved matter. The water was taken at 165 feet from the left bank, 7 feet from the surface, and 6 feet from the bottom. In November, shortly after a heavy fall of rain, and when the water was of a darker yellow, he found it to contain in the centre of the river, one foot below the surface, 51·45. Steifensand\* found the water of the Rhine, at Uerdingen, after a sudden flooding on the 29th of February, 1844, to contain 78 parts of suspended matter.† I found Rhine water, taken near the side, at Bonn, when the river was very much swollen and turbid, on the 24th of March, 1851, to contain 20·5 suspended matter, while on the 27th of March, 1852, after several weeks of continuous dry weather, and when the clear blue colour of the Rhine indicated the presence of very little suspended matter, it was found to contain only 1·73 in 100,000 parts of water. This is about the minimum quantity of suspended matter in the Rhine, and corresponds very closely with the minimum quantity in the Maes.

The suspended matter collected on the 24th of March, 1851, was, after drying, caked together, and did not soften in water. The analysis I shows its per-centage composition; II after deducting the water and organic matter.

In order to ascertain the composition of the suspended matter in the Rhine, above the Lake of Constance, I collected some of the most recent deposit of this river in the delta of this lake, in September, 1851. After drying, it appeared as a very fine, grey, sandy powder, without cohesiveness. Quartz grains, very small laminæ of white mica and black particles could be detected in it, partly with the naked eye, and partly with a magnifier. It effervesced very strongly with acid, and traces of sulphuretted hydrogen, along with carbonic acid gas, were distinctly recognizable in the gas given off. III is its composition, and IV after deducting the water and carbonates.

\* Die Entstehung und Ausbildung der Erde von Nöggerath, p. 208.

† Hartsoeker's statement that the Rhine, at the time of a high flood, contains 1-100th of suspended matter, is certainly exaggerated.



	I.	II.	III.	IV.
Silica ....	57.63	66.20	50.14	83.36
Alumina .....	10.75	12.35	4.77	7.93
Peroxide of iron ....	14.42	16.56	2.69	4.47
"    manganese .....	trace	trace	0.35	0.53
Lime .....	2.73	3.14	0.77	1.28
Magnesia .....	0.24	0.28	0.34	0.57
Potash ....	0.89	1.02	0.55	0.91
Soda .....	0.39	0.45	0.54	0.90
Carbonate of lime .....			30.76	
"    magnesia .....			1.24	
"    protoxide of iron .....			5.20	
Loss by ignition ....	9.64*			
Water ....			0.99	
Loss ....	3.31†		1.66	
	100.00	100.00	100.00	100.00

The suspended matter of the Rhine resembles in composition clay slates rich in silica, as is shown by the following analyses:—

	I.	II.	III.
Silica ....	67.91	64.51	58.91
Alumina .....	18.20	14.10	14.33
Peroxide of iron....	7.85	11.86	17.77
Lime ....	1.22		
Magnesia .....	2.73		
Potash .....	2.09		
	100.00		

I. Clay slate from Lehsten, in the Thuringer Wald, according to Frick's analysis.‡

II and III Slate for roofing, from near Arnsberg in Westphalia, according to my analyses.

\* Water and organic matter.

† This loss was chiefly owing to the presence of organic matter, for all the precipitates were coloured black by its decomposition. Hydrochloric acid dissolved 93.17 per cent. of I., and probably the whole would have been dissolved by long digestion. The suspended matter in the Rhine appears, therefore, to have a resemblance to the zeolites. This is remarkable, when it is remembered that it originates from disintegrated rocks, which, like clay-slate, contain only from 24 to 29 per cent. of substance soluble in hydrochloric acid. This can, indeed, only be in consequence of its extreme fine division, and previous partial decomposition. An idea may be formed of the fineness of these particles from the fact that more than four months elapsed before the water became perfectly clear, and that I tried in vain to separate them by filtration. A more or less advanced decomposition of rocks generally proceeds their removal by water, and it goes on by the united action of water and carbonic acid. But by this decomposition, rocks pass more or less into the soluble modification.

‡ Poggend. Ann. Bd. 35, p. 188.

Generally the alumina in clay slate preponderates in proportion to the amount of peroxide of iron present, but the two tile slates show that the iron increases as the alumina decreases, and may even exceed the latter in quantity. It is therefore easily conceivable that a clay slate, rich in iron, may be formed from the suspended matter of the Rhine when, after a certain time, it shall have become hardened to a rocky mass in the sea, either in consequence of chemical processes taking place in the sediment, or by the introduction of a cementing substance such as silica, carbonate of lime, &c. A chemical action, the partial conversion of persilicate into protosilicate of iron by the deoxydizing influence of organic remains, undoubtedly goes on in the sea; for wherever they are mixed with peroxide of iron, they cause deoxidation. Indeed the suspended matters of the Rhine are rich in organic matter. It is thus intelligible how the iron carried into the sea as peroxide is more or less converted into protoxide, the quantity of which present in clay slate is indicated by the intensity of the green colour. It is evident that this suspended matter which did not completely subside in four months, even when the water was undisturbed, cannot be deposited from the water in the few days which are required for it to flow into the sea, seeing that it is in constant motion.\* The suspended matter can only be deposited where there are no currents, as in the stagnant water left when the Rhine has been flooded.

By comparing the quantities of suspended matter and dissolved matter in the Rhine (p. 76), we obtain the following results for 100,000 parts of water:—

	Suspended.	Dissolved.	Total.
Water taken March 24, 1851 ....	20·5	11·0	31·73
Water taken March 27, 1852 ....	1·73	17·08	18·81

The carbonates which are absent in the suspended matter are found in solution. The carbonate of lime carried into the Rhine, chiefly in suspension by its tributaries, at the time of a flooding, is therefore afterwards completely dissolved.†

\* According to the experiments of Th. Scheerer (Pogg. Ann. T. 82, p. 419), the deposition of suspended matter is hastened when certain salts—alum, sulphates of copper and iron—are dissolved in the water. But since a solution of chloride of sodium behaves like pure water, it cannot be expected that the suspended matter is deposited more quickly in the sea than in rivers.

† The brooks in limestone mountains, which in dry weather are crystal clear, are rendered very turbid by rain, because the particles of carbonate of lime are so readily carried away by water. But if such turbid water falls into a large river, which, like the Rhine, is far from being saturated with carbonate of lime, the whole of this substance carried into it by the brooks is dissolved.

The springs rising in limestone are characterized by a remarkable clearness

The 3.34 parts of carbonate of lime found in the Rhine at the time of flooding amounts to only one-eighth of the quantity present in rivers which, like the Pader and the Lippe (p. 80), rise in limestone. Since these rivers have no greater opportunity of absorbing carbonic acid from the atmosphere than the Rhine, it may be assumed that there is the same quantity of free carbonic acid in both. Consequently, if eight times as much suspended carbonate of lime were carried into the Rhine as it now contains in solution, it would be all dissolved.

The comparison of the analyses III and IV (p. 76) show how minute is the quantity of carbonate of lime in suspension carried into the Rhine by its tributaries during a flooding, in proportion to its immense quantity of water. Although the water III was taken during a flooding, and IV when the Rhine was very low, the one, nevertheless, contains nearly three times as much carbonate of lime as the other.\*

It follows from the previous observations that the Rhine certainly never carries suspended carbonate of lime into the sea. If such suspended matter were carried into the sea by other rivers, it would be soon dissolved by the sea-water. It is therefore impossible to suppose carbonate of lime to exist in suspension in the open sea. Consequently, all the calcareous marine deposits, shells, and coral banks, owe their origin to the carbonate of lime dissolved in sea-water.

Since the suspended matter in the Rhine at Bonn contains no carbonate of lime, the limestone rocks traversed by this river and its tributaries can only yield the small quantities of silica, alumina, and peroxide of iron which they contain for the formation of mechanical deposits in the sea. The sandstones likewise contribute but little to these formations, since their quartz granules are not readily broken down. It is merely the cementing matter of these rocks which, after their disintegration, is washed away by water, and carried into the Rhine. As that of the old red sandstone and

during dry weather, which is recognizable even when their waters are collected in deep reservoirs. This is owing to their containing only dissolved, and no suspended carbonate of lime. On the contrary, springs rising in clay slate are not unfrequently turbid, even in dry weather, in consequence of the presence of suspended particles of clay. On this account, these brooks seldom have the clearness of those in limestone mountains, and only when their water stagnates.

\* While travelling through the Württemberg Alps during a very heavy rain, I found the brooks which rise in the adjoining limestone so extremely turbid, that I should have inferred the presence of a considerably larger quantity of carbonate of lime dissolved in Rhine water, if my analyses had not taught me that during a flood, the quantity of water in this river increases in a much higher proportion than that of the suspended carbonate of lime which is carried into it.

of the variegated sandstone is generally very rich in iron, it contributes to the great quantity of iron contained in the suspended matter of the Rhine. There are, then, chiefly the schistose and crystalline rocks and the previous clay deposits of the Rhine and its tributaries which we find in this suspended matter. This will also account for its composition approaching so closely to that of clay slate.

The suspended matter which the Rhine carries down past Bonn is chiefly derived from those rocks which it and its tributaries traverse below the Swiss lakes; for the water flowing into these lakes from above, deposits its suspended matter in them and is discharged clear.

The deposit formed by the Rhine when it falls into the Lake of Constance, differs strikingly from the suspended matter carried past Bonn, in containing more than one-third carbonate. Even if the water evaporating in the deposits formed by the Rhine leaves some carbonates of lime and magnesia, yet the quantity must be very small. The greater part of the carbonates present in these deposits has, then, been derived from suspended matter. The immense strata of limestone, and the abundance of calcareous gravel, in the Nagelflue, which are traversed by the Rhine and its tributaries, sufficiently account for the large quantity of carbonate of lime.

It might be imagined that a river which carries down carbonate of lime in suspension, would contain at least as much of this substance in solution as the rivers which rise entirely in limestone (p. 80); but the water of the Rhine at Basle contains only one-half or one-third as much carbonate of lime as these rivers. This quantity cannot be lessened by the waters of the Aar, because this river, near Berne (p. 77), contains rather more carbonate of lime than the Rhine at Basle. We must therefore conclude that the Lake of Constance, and the Rhine which flows into it, contain nearly as much of this substance as the Rhine at Basle. But in this case it must be assumed that its current above the lake is so rapid, especially during a flood, that there is not sufficient time for a perfect solution of the suspended carbonate of lime.

The source of the mica and quartz in the Rhine deposits at the Lake of Constance is to be sought in the granite, gneiss, and mica slate rocks of the Rheinwald valley, of the Luckmanier on the eastern declivity of St. Godard, and in the large quantities of mica in the Nagelflue.

The small quantity of magnesia in this deposit existing in the



form of silicate, admits of the conclusion that the mica was not magnesia, but potash-mica, which is also favoured by its silver-white lustre. Since in this mineral potash always preponderates greatly over soda, the presence of both alkalies in equal quantities in the Rhine deposit indicates also the presence of a species of feldspar. The considerable quantity of silica, and small proportion of bases combined with it, amounting to only 10%, indicates the presence of an excess of quartz granules. The small quantity of lime containing iron, leads to the conclusion that the above-mentioned black grains consist of a mineral containing protoxide of iron, perhaps garnet from the mica slate.

The minute traces of gypsum in the deposits undoubtedly originate from Rhine water which has evaporated. Organic substances have partially converted it into sulphuret of calcium, to which the evolution of sulphuretted hydrogen (mentioned at p. 122) is owing.

The deposit from the Rhine in the Lake of Constance contains the materials for the formation of calcareous mica slate, and it may easily be imagined how it should become converted into this rock when hardened by a cement and the carbonate of lime is rendered crystalline.

This deposit may be still better compared with those deposits of the Rhine which bear the name of loess, which rise to heights of 300 feet above the Rhine, in its basin and the lateral valleys. Showers of ashes, thrown out by some of the last eruptions of the volcanoes in the country surrounding the Lake of Laach, fell during the deposition of this fluviatile silt, and were interstratified with it before the period of human history.

Loess has the following composition :—

	I.	II.	III.	IV.	V.
Silica ....	58.97	79.53	78.61	62.43	81.04
Alumina ....	9.97	13.45	} 15.26	7.51	9.75
Peroxide of iron ....	4.25	4.81*		5.14	6.67
Lime ....	0.02	0.02	} 0.91	0.21	0.27
Magnesia ....	0.04	0.06		} 1.75†	} 2.27†
Potash ....	1.11	1.50			
Soda ....	0.84	1.14	} 3.33†	17.63	} + 17.63
Carbonate of lime ....	20.16			3.02	
"    magnesia ....	4.21			2.31	3.02
Loss by ignition ....	1.37				
	100.94	100.51	100.00	100.00	100.00

\* Calculated as protoxide.

† Determined by the loss.

‡ The amount of carbonates is very variable. According to analyses of loess

I. Loess from the road between Oberdollendorf and Heisterbach, analyzed by Kjerulf in my laboratory.

II. Composition of the same loess after deducting the carbonates and the loss on ignition.

III. Loess lying under the last. It differs from it, according to my analysis, in being entirely destitute of carbonates. But a comparison of II and III shows that the first loess has the same composition as this, plus carbonates of lime and magnesia. When the loess III had been elutriated, a residue remained, consisting of ferruginous quartz granules, amounting to 32·6% of the whole. Together with them, very small silver white plates of mica were visible, but in smaller quantity than in the deposit from the Rhine in the Lake of Constance.

IV. Loess from the road between Bonn and Ippendorf, according to an analysis by A. Bischof.

V. The same, after deducting the carbonates and loss by ignition.

II, III and V correspond with the composition of clay slates containing quartz. These deposits are therefore to be regarded as consisting chiefly of disintegrated clay slate and carbonates of lime and magnesia. The great similarity in the chemical composition of the clay slate and mica slate, renders it possible to imagine that this rock also may yield the material for the formation of loess. The composition of II, III and V comes so near to that of the deposit in the Lake of Constance (p. 123, IV), that, after deducting the unequal quantity of carbonates, these four may be regarded as chemically identical. This resemblance is still greater from the fact that small laminæ of mica are present in the loess III.

Between Basle and Bonn, the Rhine does not pass through any limestone. The carbonate of lime carried into it by several of its tributaries which flow through such rocks, as well as the calcareous strata in the estuary basin of Maintz, are not carried as far as Bonn in a state of suspension. The circumstances under which loess was deposited in this neighbourhood, must have been very different from those at present existing. Some violent change, such as a sudden bursting of the barrier of the Lake of Constance, in consequence of an earthquake,\* is not capable of explaining the formation

from seven different localities on the left side of the Rhine, between Maintz and Worms, made by Krockner, the quantity of carbonate of lime rises from 12·3 to 36, and that of carbonate of magnesia from mere traces to 3·2 per cent. The constituents insoluble in acids were not determined.—Liebig, *Agricultur. Chemie*, 6th ed., p. 367.

\* Lyell's *Principles*. 1st ed., p. 153.

of loess occurring in thick beds throughout the entire valley of the Rhine, where the stream is not shut in by steep rocky declivities. The quantity of water discharged by such a sudden bursting would only have amounted to about five times as much as the Rhine annually carries past Basle (p. 85). However greatly it might have been loaded with suspended carbonate of lime, its deposits would scarcely have been comparable with the existing immense body of loess. Even the opinion of Ebel, that the Rhine did not formerly flow through the Lake of Constance, but through the valley of Sarganz and through the Lakes of Wallenstadt and Zurich,\* is not sufficient to assign to the carbonate of lime in loess and the now forming deposit in the Lake of Constance the same origin, for in this case the two former lakes would have received the suspended particles of carbonate of lime. Whatever may have been the source of the carbonate of lime in loess, this can, like all other fluviatile deposits, only have been formed during a very long period and from stagnant water, for loess occurs only where the Rhine valley widens. Thus carbonate of lime cannot be a chemical deposit from stagnant water by evaporation, for in that case the suspended clay would have been first deposited, and then the dissolved carbonate of lime. But loess is an intimate mixture of these two substances.

If at some future time the Lake of Constance should be filled up by the deposit of the Rhine, suspended carbonate of lime mixed with clay will again be deposited below it, and new beds of loess formed.

The last deposits filling the widened part of the Rhine valley near Bonn, consist of a brown clay which generally does not effervesce with acids either in upper strata or in those which are lower, and rest upon sand and gravel. At one spot (near the Baumschul-Allee) the clay, five feet thick, lying upon gravel, effervesces very strongly, and this effervescence may be observed throughout the whole bed, to within a foot under the surface, where it is scarcely perceptible.† At another spot a few hundred feet distant the same characters were observed, while at other places nearer to the declivity of the valley not the slightest effervescence was to be observed. The analysis of the clay effervescing with acids yielded the following results:—

\* *Anleitung die Schweiz zu bereisen.* 2nd ed., vol. 4, p. 5.

† It is probable that the carbonate of lime in the vegetable mould has been partly washed down into the lower beds by water, and partly consumed by vegetation.

	I.	II.
Silica ....	62.30	77.34
Alumina ....	7.96	9.88
Peroxide of iron ....	7.89	9.80
Magnesia ....	0.09	0.11
Alkalies ....	2.31*	2.87
Carbonate of lime ....	13.81	
"      magnesia ....	0.53	
Loss by ignition ....	5.11	
	100.00	100.00

I. Is the analysis of the clay tolerably well separated from sand by water; but the clay was not quite free from fine quartz granules.

II. The same analysis after deducting the carbonates and the loss by ignition.

This clay very closely resembles in its composition the loess, (p. 127, IV) and likewise the Rhine deposit in the Lake of Constance (p. 123, IV). These three deposits, of which the loess is the oldest, and those from the Lake of Constance the most recent, correspond very closely in their composition when the carbonates are deducted, and this correspondence would be still greater if all the sand could be separated. As they originate from very different periods, it follows that the character of the suspended matter of the Rhine, which so closely resembles in composition the clay slates containing quartz, has been very nearly the same throughout this entire period. The only essential difference is, that these deposits are in some places quite free from carbonates, and in other places contain greater or less quantities thereof, and further that these carbonates are present not only in the oldest but also in the most recent deposits.

The water of the Elbe at Hamburg, the analysis of which is given in Chapter V, contains in 100,000 parts—

	Suspended.	Dissolved matter.	Total.
Water taken June 1, 1852 ....	0.891	12.69	13.581

The river was turbid, but the small quantity of suspended matter is remarkable. It was not sufficient for the purposes of analysis. It was of a light brown colour, and did not exhibit the least effervescence with acids.

The water of the Danube at Vienna, the analysis of which is also given in Chapter V, contains in 100,000 parts—

	Suspended.	Dissolved matter.	Total.
Water taken Aug. 5, 1852....	9.237	14.14	23.377

\* Estimated by the loss.



It was as clear as it usually is in summer; it becomes quite clear first in October and November. This considerable quantity of suspended matter is surprising at a time when the level of the river was only two feet above zero. As I had received forty-three pounds of this water, I was enabled to collect a quantity of suspended matter sufficient for analysis. On being filtered, the water becomes quite clear, but in order to collect the residue upon a small filter, four weeks were requisite. I. Analysis of the constituents soluble in hydrochloric acid. II. Constituents insoluble in this acid. III. Composition of the total matter. IV. Composition of the matter insoluble in hydrochloric acid, after deducting the loss by ignition.

	I.	II.	III.	IV.
Silica ....	5.04	39.98	45.02	80.28
Alumina . .	2.42	5.41	7.83	10.87
Peroxide of iron ....	7.76	1.40	9.16	2.81
Lime ....	.....	0.34	0.34	0.68
Magnesia ....	.....	0.42	0.42	0.84
Carbonate of lime....	24.08	.....	24.08	.....
” of magnesia ...	6.32	.....	6.32	.....
Organic matter, and probably alkalies*	.....	2.25	2.25	4.52
Loss by ignition ....	0.57	4.01	4.58	.....
	46.19	53.81	100.00	100.00

The suspended matter of the Danube differs from that of the Rhine (p. 123, I and II), inasmuch as the former contains a large quantity of carbonates, and hydrochloric acid dissolves, besides these carbonates, only 21.87% of the silicic acid, alumina and peroxide of iron, while from the latter it dissolves 93.17%. This difference depends probably upon the fact, that the suspended matter of the Rhine was collected at a time when the river was much swollen and very muddy, while that of the Danube was obtained while it was in its usual condition. In the rainy season, the brooks and rivers are rendered turbid by the unusual supplies which are carried into them from the surface of the ground. These fine earthy particles have been already exposed for a long time to the action of the atmosphere, and have advanced further in decomposition than those which the brooks and rivers in their normal

\* The quantity of the residue after ignition was so small as not to be sufficient for determining the alkalies. The black colour of the constituents separated by analysis, show likewise the presence of organic matter.

condition mechanically remove from rocks and from the detritus in their beds, and which therefore are much less chemically decomposed than the former. It is known, however, that the detritus from rocks are the more easily dissolved by acids the more decomposed they are. If, therefore, a river is during the rainy season very muddy, it contains far more of the chemically decomposed than of the undecomposed suspended matter.

The comparison of the composition of IV with that of the deposit of the Rhine in the Lake of Constance, shows a very close correspondence, which probably would have been still greater if the alkalies in the suspended matter of the Danube could have been directly determined. Since the Rhine deposits in this lake all the suspended matter which it carries along with it from the Alps, while, on the other hand, only a very small number of the Alpine rivers which join the Danube flow through lakes, the suspended matter which these streams remove from the Alps reaches the Danube. It is from these Alpine rivers, however, that the Danube receives by far the most of its water, and consequently the greatest part of its suspended matter also. Such of this matter as is found in the Danube at Vienna, is derived chiefly from the Alps; and what the Rhine deposits in the Lake of Constance, proceeds exclusively from these mountains. The matter which the Rhine deposits in the Lake of Constance, and that which the Danube contains at Vienna, may therefore be regarded almost as identical.

It remains to be ascertained, however, whether the carbonate of lime and the carbonate of magnesia of the Danube reach the Black Sea, or whether they are dissolved by the water during the long course from thence to that sea. The water of the Danube at Vienna does not contain nearly so much dissolved carbonate of lime and carbonate of magnesia as it is capable of holding. It is therefore very probable, that during the long time which the water takes in order to reach the Black Sea, the suspended portions of both carbonates are fully dissolved. Since, however, the many rivers which the Danube receives in its course from Vienna to the Black Sea, may also carry into it these carbonates in the state of suspension, it is very desirable that the suspended matter of this stream, at a short distance from its mouth, should be collected and analysed; in this way the question, so important in a geological point of view, whether this river also, like the Rhine and the Elbe, carries to the sea carbonate of lime merely in solution, may be determined.

The above investigations are only scanty commencements, but

it is very desirable that they should be extended to the analysis of the suspended matter and mechanical deposits of other rivers. It is only when a large number of such analyses shall have been made, that it will be possible to give any explanation of the origin of the sedimentary formations.

Girard\* has made an analysis of the mud of the Nile, but it is certainly incorrect. A more recent analysis, by Mr. W. Johnson,† of the mud taken near Cairo, appears to be trustworthy. After deducting the calcareous salts, the chloride of sodium, and organic matter in No. I, the per-centage composition in II is obtained.

	I.	II.
Silica ....	56·86	63·17
Alumina ....	12·12	13·47
Peroxide of iron ....	13·19	14·65
Lime ....	3·15	3·50
Magnesia ....	2·73	3·03
Potash ....	1·26	1·40
Soda ....	0·70	0·78
Carbonate of lime ....	3·12	.....
Sulphate of lime ....	1·29	.....
Chloride of sodium ....	0·36	.....
Organic matter ....	5·53	.....
	100·31‡	100·00

The composition of II has, in fact, great resemblance to that of the suspended matter of the Rhine, II (p. 123), and consequently also with the clay slate (p. 123). In the Nile mud, likewise, the peroxide of iron preponderates over the alumina. If, after a time, this mud should accumulate in thick beds, the peroxide of iron in the lower layers, removed from atmospheric influence, would be converted into protoxide by the large quantity of organic matter which it contains. If these beds, hardened in course of time, are elevated above the sea, and meteoric water, loaded with atmospheric carbonic acid, penetrates through them, the protoxide would be dissolved, and again deposited, partly in the form of carbonate, partly as hydrated protoxide, in fissures or beds. It is thus conceivable how strata, originating from such deposits, may, after a while, gradually be

\* Observations sur la Vallée d'Egypte, p. 64.

† Quarterly Journal of the Chem. Soc. Vol. 4, p. 143.

‡ Only 32·6 per cent. of Nile mud was dissolved by hydro-chloric acid, containing only 0·76 silica. It is, perhaps, possible that this different behaviour towards acids in the Nile mud and the Rhine mud depends upon the latter having been analysed shortly after its deposition from the water, while the Nile mud had laid, perhaps, for many years, and the silicates had passed into the insoluble modification.

deprived of a large part of its iron, and approach the normal composition of clay slate.

According to the investigations of Ehrenberg,\* the mud of the following rivers contains infusoria:—

In every second they carry along with them, of solid matter,		In these solids are contained of infusoria,	
	Cubic Feet.	Cubic Feet.	Per Cent.
The Mississippi, at Memphis,	147 ....	2 to 3 or	1·4 to 2
The Nile ....	130·9 ....	6 „ 13 „	4·6 „ 10
The Ganges ....	557 ....	69 „ 139 „	12·4 „ 25

In the mud of the Mississippi Ehrenberg found 44 *Polygastrica*, 17 *Phytholithania*, and 2 fresh-water *Polythalamia*; in that of the Nile, 160 *Phytholithania*, as well as lamellæ of mica.

Analyses of fluvial deposits in valleys unaltered by cultivation, may be connected with the above. Colonel Fremont† has given some of soils in the valleys of the Rocky Mountains:

	I.	II.	III.
Silica ....	68·55	72·30	70·81
Alumina ....	7·45	6·25	10·97
Peroxide of iron ....	1·40	1·20	2·21
Lime and magnesia .....	.....	.....	1·38
Carbonate of lime ....	8·51	6·86	.....
„ magnesia ....	5·09	4·62	.....
Phosphate of lime ....	.....	.....	1·01
Organic matter ....	4·74	4·50	8·16
Water and loss ....	4·26	4·27	5·46

I. Soil in the river bottom near Fort Hall, situated in the neighbourhood of the confluence of Portneuf river with Lewis's fork of the Columbia river.

II. Powder river soil.

III. Grand Rond soil.

After deducting the carbonates, phosphates, organic matter, and water, there remain:

	I.	II.	III.
Silica ....	88·56	90·66	82·94
Alumina ....	9·63	7·84	12·85
Peroxide of iron ....	1·81	1·50	2·59
Lime and magnesia ....	.....	.....	1·62
	100·00	100·00	100·00

\* *Berichte der Berliner Acad.* 1851, p. 324.

† Report of the Exploring Expedition to the Rocky Mountains in the year 1842, &c. Washington, 1845, pp. 163, 178, and 179.



These quantities approach those in the Rhine deposits of the Lake of Constance (p. 123); and as carbonates are present in the deposits I and II, it may be inferred that those formed by the rivers of the Rocky Mountains originate in the same kind of rocks as that formed by the Rhine (p. 125). These deposits do not appear to have been examined for alkalies, but the loss in the analyses shows that alkalies are certainly present. It is possible that the Nile and the rivers in the Rocky Mountains, No. III excepted, carry along suspended carbonate of lime as well as the Rhine above the Lake of Constance. The possibility that the carbonate of lime in fluvatile deposits may originate in the scales of infusoria, should not be overlooked, in which case the carbonate of lime dissolved in the water would have furnished the material. This point must, however, be decided by microscopic investigations.

The black earth, or tschornasems of Central and Southern Russia, appears to be, according to Murchison, &c.,\* a subaqueous formation. This fine silt is, for the extent of its uniformity in colour and composition, without parallel in Europe. It is found at all levels in European Russia, sometimes on plateaux, as on the right bank of the Volga, high above the adjacent plains, in various parallels, from  $56\frac{1}{2}^{\circ}$  north latitude to the high grounds extending to Saratof, and at heights of not less than 400 feet above the valleys.

The analysis of this earth is as follows:—

	R. Phillips.†	Fayen.‡	Hermann.§
Silica acid .... ..	74.57	77.93	82.05
Alumina ... ..	14.42	12.41	10.49
Oxide of iron ... ..	7.48	6.12	6.44
Lime ... ..	1.71	0.89	1.02
Magnesia ... ..	.....	1.33	
Traces of humic acid, sulphuric acid, chlorine, &c. ....	1.82		
Alkaline chloride ... ..	.....	1.32	
	100.00	100.00	100.00

This earth differs from loess, in the fact that it contains no carbonates and no terrestrial and fluvatile remains; whilst the

\* The Geology of Russia. 1845, Vol. 1, p. 557.

† After deducting 6.4 per cent. of organic substances.

‡ After deducting 6.95 per cent. of organic substances.

§ After deducting 10.42 per cent. of organic substances, and 4.08 per cent. of water. Other two specimens of this earth, examined by Hermann, had nearly the same composition. Journ. für pract. Chemie, T. 12, p. 290.

latter is abundantly filled with terrestrial and lacustrine shells in perfect preservation. After deducting the carbonates from the loess (p. 127, II), there is obtained a composition which is very near to that of the tschornasems, according to the analyses I and II.\* Murchison thinks it highly probable that the tschornasems have, to some extent, been derived from the destruction of the black turassic slate, so uniform in its colour over all Northern and Central Russia, and that it could not have been formed in the present period. This view is, from the large amount of bituminous matter contained in this slate, very probable.

Sir G. Wilkinson† investigated the changes which the alluvial deposit of the Nile produces in the levels of the land, and in its bed. K. G. Zimmermann made some interesting observations on the deposits of the Elbe, in the island Grasbrook, near Hamburg, during historic periods.‡

\* According to the analyses of some specimens of the black earth from Southern Russia, by E. Schmidt (*Journ. für pract. Chemie.* T. 59, p. 129), their composition approaches for the most part that of the clay-slate.

† *Edinb. New Phil. Journ.* Vol. 28, p. 212. The bed of the Nile, as also the land of Egypt, undergo a gradual increase of elevation, varying in different places according to circumstances, and always lessening in proportion as the river approaches the sea. This increase of elevation, in perpendicular height, is much smaller in Lower than in Upper Egypt, and in the Delta it diminishes still more; so that, according to an approximate calculation, the land about Elephantine, or the first cataract (lat.  $24^{\circ} 5'$ ) has been raised 9 feet in 1700 years; at Thebes (lat.  $25^{\circ} 43'$ ) about 7 feet; and at Heliopolis and Cairo (lat.  $30^{\circ}$ ) about 5 feet 10 inches. At Rosetta, and the mouths of the Nile (lat.  $31^{\circ} 30'$ ), the diminution in the perpendicular thickness of the deposit is lessened in a much greater decreasing ratio than in the straitened valley of Central and Upper Egypt, owing to the greater extent east and west, over which the inundation spreads; and there the elevation of the land, in the same period of 1700 years, has been comparatively imperceptible.

‡ *Neues Jahrbuch für Mineralogie, &c.* 1852, p. 193. He found in the above-named island three beds of shells, from  $\frac{1}{2}$  to  $1\frac{1}{2}$  feet thick, which were separated by beds of marsh clay 8 inches thick. The upper bed contains only fresh-water shells, mixed with fragments of building stone and pottery. The second bed contains only a few fragments of bricks, but among the fresh water shells, lying close together, are many marine species. Under this shell-bank lies a bed of marsh clay, and beneath this, a bed of broken ash and pine-wood, a foot in thickness, covering the lowest bed of shells which has yet been reached. The latter consists chiefly of fresh-water shells, although marine species are frequently found, but only in such a way as to render it probable that they have been accidentally carried there by floods. He infers from these facts, that before the deposition of the upper banks, the sea was so near to the island that marine shells might have been thrown upon it; while, at the present time, the highest tides can no longer bring them so far; and further, that the Elbe formerly fell into an arm of the North Sea, between Hamburg and Harburg, and that the numerous islands in the Elbe were formerly sand-banks originating in a delta formation. But at that time there must have been human habitations near the shore, as is proved by the remains of building stones. Since the uppermost shell-bed is nearly 12 feet above the present level of the Elbe, Zimmermann is of opinion that this river must have fallen more than this distance during historic periods.

With regard to this conclusion it must be remarked, that rivers deepen

With regard to the grouping of strata in deltas, Lyell\* remarks, that if a lake be encircled on two sides by lofty mountains, receiving from them many rivers and torrents of different sizes, and if it be bounded on the other sides, where the surplus waters issue by a comparatively low country, the strata formed would be divisible into two principal groups. The older comprising those deposits which originated on the side adjoining the mountains, and would be composed for the most part of coarser materials, containing many beds of pebbles and sand, dipping at a considerable angle, these would be associated with beds of finer ingredients. The newer group consisting of beds deposited in more central parts of the basin, and towards the side furthest from the mountains, would be composed of finer particles and would be horizontal, or very slightly inclined. He alleges these diverse causes which produce the diversity here alluded to between the two great members of such lacustrine formations. In deltas where the causes are more complicated, and where tides and currents partially interfere, the above description would only be applicable, with certain modifications.

Natural divisions are also occasioned in deltas by the interval of time which separates annually the deposition of matter during the periodical rains, or melting of the snow upon the mountains. The deposit of each year may acquire some degree of consistency before that of the succeeding year is superimposed. A variety of circumstances also give rise to slight variations in colour, fineness of the particles, and other characters, by which alternations of strata, distinct in texture and mineral ingredients, must be produced.†

their beds in the upper part of their course the more considerably the more steep is their fall; but that near their discharge into the sea, and as far above as they flow through flat land, the reverse is the case; they partially deposit here the matter which they have collected higher up. If the Elbe had formerly fallen into an arm of the sea between Hamburg and Harburgh, its level at this spot was as much lower as its present fall to the North Sea. Disregarding this very slight fall, the water of the then existing arm of the sea would, at the time of ordinary tides, have risen 12 feet, for the tides of the North Sea now rise as much before the mouth of the Elbe. At the time of spring-tides, however, it rises much higher. These facts are sufficient to afford a simple explanation of the deposition of these sand-banks, which now stand nearly 12 feet above the present level of the Elbe.

\* Loc. cit., pp. 271 and 273.

† Interesting investigations have been recently made with regard to the sedimentary formations in the Alpine lakes. *Terrain erratique alluvien du Bassin du Léman, et de la vallée du Rhône de Lyon à la mer*, par R. Blanchet. Lausanne, 1844. *Notice sur la Carte du fond des Lacs de Neuchâtel et Morat*, par A. Guyot. Neuchâtel, 1846. On the accession of new land at the mouth of the Rhône, at the upper end of the Lake of Geneva, since the historic era, see Lyell's *Principles*, p. 253. At the entrance of the Rhine into the Lake of Constance, the alteration of the course of this river within the delta which it has

Donati\* after dredging the bottom of the gulph of Trieste and the Adriatic opposite Venice, discovered the new deposits to consist partly of mud and partly of rock, the rock being formed of calcareous matter incrusting shells. He also ascertained, that particular species of testacea were grouped together in certain places, and were becoming slowly incorporated with the mud or calcareous precipitates.

C. H. Davis, in an excellent memoir,† shows that the natural inequalities in the level of the sea bottom must to some extent cause the suspended matter to accumulate in great quantities in particular places, in consequence of their interrupting the stream, and not only taking up a portion of its burden, but likewise occasioning the eddies, which are especially favourable to deposition. The inequalities need not be very great. Small impediments at the mouths of harbours, or in rivers, serve the purpose of a nucleus. A tidal current freighted with suspended matter, and eddying round a bold point, is interrupted and changed in its course by the projecting tongue or prominence at which it turns, and will leave there constantly a part of its burden, this prominence serving as a nucleus to a shoal or bar joined to the land, in the same manner as the inequalities of the bottom to the insulated shoal at sea.‡ The subsequent gradual elevation of the shoal above the water is due to the influence of the winds.

The normal currents of the ocean may take the place of the tidal currents, and exhibit the same effects. The constant current flowing into the Mediterranean may be cited as a striking example. At the rock of Gibraltar this current divides into two branches, one of which enters the Bay of Gibraltar, while the other passes to the eastward of the rock; and the conflicting action of these two streams has built up the long and narrow ridge of sand, known by the name of the neutral ground, that unites the fortress to the

formed, is distinctly traceable. This lake formerly extended into the Rhine valley beyond Altstetten. Walchner's *Geognosie*, 2nd Edition, p. 776. The land round this lake, to a distance of several miles, is covered with large masses of Alpine boulders. These occur even at heights of 1465 feet above the sea—and, indeed, upon the German side; whence it follows that they must have been carried there at a time when the Lake of Constance was not in existence. Frommherz, in the *neuem Jahrbuche für Mineralogie*, &c. 1850, p. 641.

\* Lyell. *Loc. cit.*, p. 208.

† On the geological action of the tidal and other currents of the ocean. From the *Memoirs of the American Academy of Arts and Sciences*. New Series. Vol. IV.

‡ This mode of accumulation of suspended matter is familiar to engineers. In the rivers Aar and Rhone, walls projecting into the current are built expressly to obtain a new soil by creating eddies, the sedimentary matter being collected in large quantities by these eddies in one place.



Spanish Peninsula. The large bank to the eastward of this ridge is an instance of *bay deposit*.

Tides and delta deposits are incompatible with each other; where there is a regular tidal or normal current of any consequence there can be no delta formed. Such a current will always be a characteristic feature of those wide bays and river outlets where deltas do not exist.\* At the mouths of all those rivers most distinguished for their deltas, as the Mississippi, the Nile, the Po, the Rhone and the Orinoco, there is little or no tide; while, on the other hand, there are tides of a marked and decided character at the mouths of other rivers, equally strong and muddy in their currents, and magnificent in their dimensions, but having no delta deposits, as the Canton, the Guayaquil, the Amazon, the Paraguay, and others emptying into the Rio de la Plata, the rivers of Western Europe, and all the rivers on the eastern coast of North America, north of Florida.

Deposits upon the ocean border are only made by the current of the flood-tides. In the sounds and bays, the ebb tide may also leave its burden, since in its retreat it may not only meet with obstructions, but must press upon the land in some parts, precisely as the advancing flood does upon the exterior coast. In general, as the deposit of the flood is made on the shore in the direction of its progress, so the deposit of the ebb is buried in the bosom of the ocean. The former furnishes the material for the alluvial deposits above water; the latter supplies the substances found in the depths of the sea.

By many examples which are found on the shores of America respecting the deposits of sand, Davis shows that the consequence of conflicting currents is the condition most favourable to a large deposit. As to the shores of Europe, we there find deposits of sand of remarkable extent. Holland is the most interesting, in many respects, of all similar formations. The narrowness of the English Channel, by creating rapid currents, forbids deposits there, except in those small bights and bays where the water becomes still, or expends its force in eddies. But when, after passing the Channel, the sea expands, the circumstances are again suited to the deposition of its burden, especially on the side concave to its axis, or in other words, having the bay form, which is the situs of the Netherlands and the Peninsula of Jutland. The convergence of the tide-waves in the North Sea and English Channel, is a very

\* This fact, of the absence of deltas where there are regular tides, is distinctly stated by De la Beche in his Manual.

conspicuous feature of this region. Professor Whewell has, in his valuable "Researches on the Tides," endeavoured to combine all the facts into a consistent scheme, by dividing this ocean into two rotatory systems of tide-waves; one occupying the space from Norfolk and Holland to Norway, and the other the space between the Netherlands and England. On the coast of Jutland there is a vanishing point of the tide, which he endeavours to explain by the motions of the former system.

Throughout this region there is a correspondence between the height of the tide on the one hand, and the form of the land and amount of the deposits on the other. The greatest range of the tide between Brest and Dunkirk varies from 30 to 16 feet. But after passing the narrow limits of the Channel, it descends, in proceeding along the coast of the Netherlands, to 9, 6, and 3 feet. Finally, on the north of Jutland, the tide ceases to rise altogether; a state of perfect uniformity is produced by the conflicting currents. In this conflict of tide-waves coming from the north with those advancing through the British Channel, by which the latter are forced over upon the eastern shore, retarded in their progress, and finally repelled,—in these rotatory systems or eddies upon a grand scale of the tidal currents,—in the bay form of the shore, and in the gradually-decreasing height of the tide taken as an exponent of its strength, we have a combination of all the circumstances most favourable to alluvial and subaqueous deposits.

Hitherto, as Davis rightly remarks, the tides have been regarded chiefly as an astronomical problem; but if the views brought forward in his valuable memoir are correct, they must hereafter be treated also as a strictly geological problem, applicable to all ages of the earth's history. The estimation of the action of the tides, or in other words, the influence in this manner of the moon upon the earth's surface, is a new application of the law of gravitation.

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## CHAPTER IX.

### CHEMICAL DEPOSITS.

DEPOSITS in fissures between plains of stratification and in drusy cavities, cannot have originated from ascending springs, (see

p. 72); for their channels must always be entirely filled with water. It is only when water flows down the walls of these channels that the conditions for deposition and the formation of dykes and veins are fulfilled.

We find mineral springs which have issued from the same spot during inconceivable periods of time, depositing, like those in the neighbourhood of the Lake of Laach, immense quantities of iron ochre. As their channels are very narrow, they would long since have been stopped up, if only the millionth part of the hydrated oxide of iron which is deposited upon the surface had been deposited in the channels. So large a quantity of carbonate of lime and carbonate of iron is brought to the surface at Neusalzwerk, near Prussian Minden, that the boring might have been stopped up by it in six days. Even if only a minute quantity of it had been deposited, it would long since have been stopped up.\*

The impossibility of the deposition of solid matter by the water of ascending springs in their channels may be readily conceived. The conditions under which deposits take place—evaporation of water, escape of carbonic acid, cooling of hot water, higher oxidation of iron and manganese—cannot be imagined to take place in the channels of ascending springs. This deposition does not take place until the water *has reached* the surface, where more or less considerable layers are formed. It is from the presence of such layers that the previous existence of springs may be inferred, when they are no longer active.

Our present ascending springs issue either in valleys or upon the declivities of mountains, because it is only here that the conditions of their ascent from below, in consequence of the pressure of water in the surrounding heights, are fulfilled. The same was also the case with previously existing and now extinguished ascending springs. We cannot, therefore, expect to meet with any deposits from springs upon the highest points of a district. If, however, they should be met with, this would warrant the conclusion that considerable changes had taken place in the configuration of the earth's surface at these points.

Some geologists, who ascribe the filling up of veins and clefts to ascending springs, go even so far as to regard the depositions in drusy cavities as being formed by ascending hot water which has penetrated through whole mountains. Such an hypothesis is altogether irreconcilable with hydrostatic laws. Whence can the

\* Bischof, German ed., T. 2, p. 814, &c.

immense quantities of water which must have flowed from these ascending springs during long spaces of time have been derived?

Deposits from springs, however insignificant they may be in themselves, are of great importance in geology; for they show what water is capable of dissolving, and, under other conditions, of depositing. They show more than the examination of spring waters; for constituents which are present in such minute quantities that they can no longer be detected by analysis, are easily recognized in these deposits. For example, when carbonate of iron is present in the water of a spring in such minute quantities that the most delicate reagents fail to show its presence, this iron may be detected in the channels through which the water runs off uninterruptedly. Here the iron must become perceptible, in consequence of the conversion of the carbonate into hydrated peroxide by atmospheric oxidation.

Had not Berzelius analysed the deposits (*sprudelsteine*) from the Carlsbad springs, we should perhaps still be ignorant of the occurrence of fluorine, of phosphoric acid, and of strontia in the water of mineral springs. We are likewise indebted to Walchner's extended examination of ferruginous ochery deposits for the discovery of copper, of arsenic, and of antimony in spring waters. It cannot be doubted that many more metals will be found in such waters, when more attention is directed to this subject.

The analysis of the Saischütz water is an example of the results of such investigations, and shows that careful analyses of mineral waters afford a favourable prospect in this direction. Berzelius\* found in this water traces of tin and copper; their presence is of especial importance, as this spring rises from a decomposed crystalline rock, where the olivine, which appears to yield the magnesia to the water, likewise contains traces of these two metals.

Moreover, it is possible, from the character of the deposits, to infer what were the conditions of their formation; and they may be traced to the evaporating or cooling of water, the volatilization of gaseous constituents, chiefly carbonic acid, or the further oxidation of fixed constituents. Deposition by evaporation can only take place when water stagnates, or when it trickles down the walls of fissures and evaporates during its passage. But the surface over which the water spreads itself in this case must be so large, that the evaporation removes water more rapidly than it is replaced. Deposits are readily formed from springs whose

\* Poggend. Annal., T. 4, p. 150.



temperature considerably exceeds that of the atmosphere, when evaporation and cooling are capable of effecting a separation of dissolved substances. In springs whose temperature, at least in summer, is lower than that of the atmosphere, it is only after a long time that evaporation can cause a deposition.

*Siliceous deposits from warm springs.*

The most considerable of these is the siliceous tufa of the Geysers, in Iceland, the composition of which is stated as follows :—

	Klaproth.*	Kersten.†	Forchhammer.‡
Silicic acid ....	98·00	94·01	84·43
Alumina ....	1·50	1·70	3·07
Peroxide of iron ....	0·50	trace	1·91
Magnesia ....	.....	.....	1·06
Lime ....	.....	.....	0·70
Potash and soda ....	.....	.....	0·92
Water ....	.....	4·10	7·88
	100·00	99·81	99·97

Forchhammer ascribes the considerable discrepancy between his analysis and Kersten's to a variability of the kinds of sinter deposited at different times.

The deposition of siliceous sinter is a joint effect of cooling and evaporation. By cooling alone, about one-tenth of the silicic acid separates; for the water which Forchhammer received in sealed flasks was cloudy, and left that quantity of silica on the filter. Geyser water contains in 10,000 parts—

	Forchhammer.	Pfaff.§
Silicic acid ....	4·09	8·00
Soda ....	1·32	.....
Chloride of sodium ....	1·68	1·68
Sulphate of soda (magnesia) ....	0·62	1·32
Sulphate of lime ....	0·34	.....
	7·96	11·00

\* Beiträge zur chemischen Kenntniss der Mineralkörper, T. 2, p. 109.

† Schweigger's Journal, T. 66, p. 27.

‡ Poggend. Annal., T. 35, p. 350.

§ Amtlicher Bericht über die 24th Versammlung deutscher Naturforscher in Kiel. 1846, p. 183.

According to the former analysis, this water contains silicate of soda, and the minute quantity of magnesia may likewise be combined with silicic acid.

The island of St. Miguel, one of the Azores, is rich in siliceous deposits from warm springs. Hochstetter\* examined a mineral from the island of Terceira, which is undoubtedly a deposit from warm springs, and consisted of 77.05 silicic acid and 1.07 peroxide of iron, with 22.2 of disseminated sulphur. As aqueous vapours impregnated with sulphuretted hydrogen are evolved where this mineral is found, it cannot be doubted that the sulphur originates from this source.

Dieffenbach and Hooker† found in the interior of New Zealand hot springs which form deposits resembling chalcedony. According to the former‡ also, there are along the delta of the Waikato hot springs rising on the declivities of mountains whose waters deposit a sinter containing 75% of silica. There is also a cold silicifying spring in the neighbourhood of Cape Maria.

It is very probable that on a closer examination all these siliceous deposits will be found to contain minute quantities of bases.

#### *Siliceous deposits from cold springs.*

Deposits of silica, with but small quantities of bases, such as are found in the above-mentioned instances at the issue of some hot springs, do not appear to be formed by cold springs. The reason of this is probably the minute quantity of silica present in the water of cold springs, on account of which its separation cannot take place until the water has completely evaporated. Partial evaporation and cooling, which so frequently cause the separation of the larger quantities of silica present in the water of hot springs, are no more capable of effecting this separation from the water of cold springs than the volatilization of the carbonic acid, which is not a solvent for silica.

Nevertheless, some cold springs form deposits tolerably rich in silica, but it is in combination with larger quantities of bases than the deposits formed by hot springs. An abundant deposit was found in the island Flores, the most western of the Azores, forming thick strata at some distance from the issue of the springs.

\* Journ. für prakt. Chemie, T. 25, p. 376.

† L'Institut. 1845. No. 593.

‡ Ibid. 1845. No. 617.

Dilute hydrochloric acid dissolved only 13% of peroxide of iron and a little lime and alumina from this deposit; the insoluble part consisted of—

			Oxygen.
Silicic acid	....	67.6	35
Peroxide of iron	....	21.0	6.4
Alumina	....	10.2	4.7
Lime	....	1.0	0.3
			11.4
			99.8

The oxygen of the silica is very nearly the triple that of the bases, so that the insoluble part might be considered as an actual neutral silicate. This deposit is remarkable on account of the considerable quantity of silica, and also because it proves the solubility of a double silicate of alumina and peroxide of iron, or perhaps originally protoxide. A deposit from mine water, formed in the mine Himmelfahrt, near Freiberg, originates from the dropping of the tubes of the pumps upon the neighbouring gneiss and has a thickness of 2 to 4 lines, and is scarcely separable by the hammer. According to Kersten,\* it consists of—

Silicic acid	....	18.98
Peroxide of iron	....	22.90
Oxide of manganese	....	25.01
Water	....	33.00
		99.89

We have here an example of the mode in which siliceous formations may originate by the total evaporation of ordinary water containing only a very small quantity of silica in solution. It suggests that the same process must take place when such water trickles so slowly down the sides of a mountain fissure that the whole of the water evaporates in the meantime. It is to this process, without doubt, that we must ascribe the formation of the very frequent quartz dykes and veins in rocks, as I have already shown.† It depends upon the nature of such water, whether pure quartz

\* Journ. für pract. Chem. Bd. 22, p. 1.

† Neues Jahrbuch. für Mineral &c. 1844, p. 257.

dykes or such as contain iron or manganese are formed. As the fresh water filtering through rocks generally contains too little carbonic acid to take up more than very small quantities of peroxide of iron and manganese, the reason is obvious why these waters form the purest quartz dykes and the clearest rock crystal. The numerous siliceous formations (chalcedony, hornstone, amethyst, rock crystal, &c.) in the drusy cavities of amygdaloid rocks present exactly the same relations. They have likewise originated from the water filtering through the rocks.

*Deposits from hot springs consisting chiefly of carbonate of lime, or of this and hydrated oxide of iron.*

We will first refer to the deposits from the brine at Neusalzwerk, which rises from the boring, 2,160 feet deep, with a temperature of 91° F. This brine, which flows at the rate of a cubic foot in a second, forms a considerable deposit of carbonate of lime and hydrated peroxide of iron in its open discharge-channel, which has a length of 2,940 feet, and empties itself into the Werra. At points where the brine falls in small cascades, and presents abundant surface of contact with the atmosphere, by which the escape of carbonic acid and the higher oxidation of the iron is facilitated, the deposit had, at the time when I saw it, a height of nearly three feet, and yet only five years had elapsed since the discharge had commenced. The deposit forms globular and reniform masses, of a more or less ochrous brown colour, which have the greatest resemblance to brown hematite, and show decidedly that this has been produced in the same way.

The essential constituents of this deposit are hydrated peroxide of iron and carbonate of lime in very unequal proportions. The deposits in the discharge-channel contain the greatest quantity of iron near the boring, and the least near the Werra. Therefore the former have a darker, and the latter a lighter ochre brown colour; if this channel were still longer, almost pure carbonate of lime would be deposited at last. Therefore, water, which contains carbonates of lime and protoxide of iron may, when it passes for a long distance in contact with the air, finally deposit pure carbonate of lime. This is in itself evident, since the deposition of the iron is the result of a double action—escape of carbonic acid, and simultaneous oxidation of the protoxide of iron. On the contrary, the deposition of carbonate of lime results only from the escape of half the combined carbonic acid.



If this brine had a course twice as long, and then flowed down into fissures in rocks, it would deposit in them a carbonate of lime containing only traces of iron. It is the more easy to comprehend such an origin of the dykes of calcareous spar, from the circumstance that even the purest and whitest calc-spar always contains traces of iron. Finally, we understand how pure calc-spar may be produced by the decomposition of silicates containing lime and protoxide of iron (augite, hornblende, labrador, &c.), by means of carbonic acid, when the carbonates formed are dissolved by water which flows for a long distance in contact with the atmosphere. It depends upon the temperature of such water, whether more or less carbonate of lime is deposited at the same time as the hydrated peroxide of iron; for the higher the temperature, the more rapidly does the half-combined carbonic acid of the bicarbonate escape when the water comes into contact with the air and is cooled more or less rapidly. If the temperature is the same as that of the atmosphere, or still lower, there is at first scarcely any carbonate of lime deposited, but only hydrated peroxide of iron, as is shown by ochrous deposits from cold springs, to be mentioned subsequently. Therefore, under these circumstances, beds or veins of brown iron ore, and afterwards of pure calc-spar, may be formed from the same water. The higher or the lower the temperature of the water, the more or less rapid its cooling, the greater or less abundance of bicarbonate of lime and protoxide of iron, and the different proportions in which these compounds occur,—all these circumstances may give rise to the most varied deposits of these substances as regards their relative quantity.

The brine of Neusalzwerk brings annually to the surface 1 807,883 pounds, or 10,145 cubic feet, of carbonate of lime, and 139,036 pounds, or 462 cubic feet, of hydrated oxide of iron. Where such quantities of mineral substances are brought to the surface, there is material enough for the formation of the thickest beds and dykes of calc-spar and brown iron ore, when such waters flow for thousands of centuries and form deposits. The issue of this brine lies 88 feet above the Werra. If open fissures in the rocks proceeded from thence, and the water trickled down their sides, there would still be such veins formed.

Considerable deposits from brines which have been worked from time immemorial, are by no means uncommon. Thus, to name only one example, the salt spring of Salzkotten, the tem-

perature of which is  $66^{\circ}$  F., is surrounded by a hill of ferruginous lime sinter, which was without doubt deposited from the brine before it was made use of. The same sinter is still deposited in the graduation houses. From the height of this hill, it may be inferred that this brine spring is of great antiquity, and that it was not opened in the first instance by boring.

While we find at Neusalzwerk a communication opened artificially between great depths and the surface, in Carlsbad and other places this has been effected naturally. Such springs have without doubt risen in former times at many places where they are now no longer found, but only the indications of their previous existence, in the form of considerable layers of carbonate of lime and brown iron ore.

The so-called sprudelstone, from the Carlsbad hot springs, throws much light upon the deposits in question, partly because it forms enormous beds, partly because, as the analyses of Berzelius\* show, its composition is under different circumstances very variable.

These hot springs issue from openings in a limestone which is formed from the water itself; for wherever it flows, it deposits sinter of compact and crystalline texture, in proportion as the carbonic acid escapes.†

Berzelius found that the substances dissolved by carbonic acid in the Carlsbad hot springs—carbonates of lime, strontia, protoxide of iron, phosphates of lime and alumina, and fluoride of calcium—crystallize out, when the carbonic acid escapes, independently of the diminution of the liquid, but that the magnesia and silicic acid were not deposited until the evaporation had taken place. This sufficiently proves what are the constituents of the deposits.

The sprudelstone is partly white, partly brown, and partly consisting of alternating white and brown layers. The brown contains a considerably larger quantity of peroxide of iron than the white, which is sometimes quite free from it. This difference presupposes either that there is a difference in the quantity of iron contained in the water, or that sometimes the atmospheric air has a greater influence than at others, and that in those cases a larger quantity of protoxide of iron is peroxidized.

The analysis of different specimens of sprudelstone, by Berzelius, gave the following results:—

\* Gilbert's Ann. Vol. 74, p. 123.

† With regard to the extent of these deposits, see Bischof, German edition, Vol. 1, p. 887.

	I.	II.	III.
Carbonate of lime ....	97.00	96.47	43.20
„ of strontia ...	0.32	0.30	.....
Phosphate of lime ....	0.59	0.06	.....
„ of alumina } .....		0.10	0.60
„ of iron ....		0.43	19.35
Basic phosphate of iron ....	.....	.....	1.77
Carbonate of iron ....	.....	.....	12.13
Fluoride of calcium ....	0.69	0.99	.....
Silicic acid ....	.....	.....	3.95
Water ....	1.40	1.59	9.00
	100.00	99.94	100.00*

I. A brown fibrous and very hard sprudelstone, used for the manufacture of ornaments.

II. Sprudelstone which is deposited upon the tin boilers in which water is evaporated for preparing the Carlsbad salt.

III. A peculiar kind of sprudelstone, which is formed round an opening in the crust where the water constantly drops, and is exposed to simultaneous oxidation and evaporation. Although the fracture of this stone was reddish brown, it contained a considerable quantity of protoxide of iron.

A fourth sprudelstone, having a white colour, a granular or delicate fibrous fracture, contained a minute quantity of fluo-silicate of potassium.

The deposit formed by the water (temp. 113° F.) of Cæsar's bath, at Mont Dore, in Auvergne, consists, according to Berzelius,† of a mixture of hydrated peroxide of iron, persilicate of iron, and basic perphosphate of iron, combined with water. The calcareous tufa from the warm spring of St. Allyre, near Clermont, in the Auvergne, consists, according to him,‡ of carbonates of lime and magnesia, phosphates of lime, magnesia, and protoxide of manganese, making together 0.52% and 6.8% of gelatinous silicic acid.§

The deposits from the warm spring (115° 25 F.) of the Kesselbrunnen, at Ems, are especially worthy of notice, because they

\* There is a misprint here, which decreases the total sum by 10. One of the constituents, perhaps the carbonate of lime, has been stated too low by 10 per cent.

† Loc. cit., p. 298.

‡ Ibid., p. 299.

§ With regard to the remarkable circumstances accompanying the formation of this tufa, see German edition, Vol. 1, p. 891.

contain the metallic oxides but recently discovered in spring-waters.

	III.	IV.
Carbonate of lime ... ..	7.9512	92.3250
„ magnesias ... ..	1.6341	7.0010
„ strontia ... ..	0.0831	0.0082
„ baryta ... ..	0.0806	0.1481
Sulphate of baryta ... ..	0.3894	.....
Phosphate of alumina ... ..	2.5707	0.1959
Phosphoric acid combined with peroxide of iron...	2.4332 }	
Peroxide of iron ... ..	39.7260	0.1434
Peroxide of manganese ... ..	0.2849	0.1134
Arsenic acid combined with peroxide of iron ...	0.1189	trace
Oxide of copper ... ..	0.0419	.....
„ lead ... ..	0.0764	.....
Silica dissolved by hydrochloric acid ... ..	3.1471	.....
Residue insoluble in hydrochloric acid (silica, clay, sand) ... ..	32.6820	0.1120
Organic matter and water in the clay ... ..	2.2158	.....
Water combined with peroxide of iron ... ..	6.5647	.....
Fluoride of calcium ... ..	.....	trace
	100.0000	100.6470

### III. Deposits near the springs.

IV. Deposits of calc-sinter at a greater distance from the spring.\*

With regard to the deposition of carbonate of lime and peroxide of iron at different distances from the spring, the same relations are observed here as in the case of the brine springs at Neusalzwerk (p. 146). The comparison of III and IV shows that the protocarbonate of iron is deposited in consequence of oxidation, together with phosphoric acid and the extremely small quantities of arsenic acid; that the bicarbonate of baryta cannot long exist in the water together with sulphate of soda; that the bicarbonate of manganese resembles in its characters the corresponding bicarbonates of the alkaline earths more closely than the corresponding ferruginous salt; and, finally that, as was already remarked, the bicarbonate of lime is much more rapidly decomposed than the bicarbonate of magnesia.†

\* Fresenius, in the Jahrbücher des Verins für Naturkunde in Nassau. Heft. 7, p. 165.

† For 1 part arsenic acid there are 334 parts peroxide of iron. Assuming that these constituents are present in the water in the same proportion, it follows that in every pound of water there is  $\frac{1}{25000}$  arsenic acid. With regard to the



Deposits from the warm springs (158° F.) of the Kochbrunnen at Wiesbaden :—

	I.	II.	III.
Carbonate of lime ....	13·663	90·736	94·339
„ magnesia .....	trace	0·497	0·676
„ protoxide of manganese....	trace	trace	0·265
Sulphate of lime ....	trace	0·013	0·186
„ baryta .....	0·164	trace	0·052
„ strontia .....			
Peroxide of iron .....	61·103	4·884	2·2 22
Oxide of copper .....	trace	trace	trace
Alumina ....	trace	trace	trace
Arsenic acid .....	1·736	0·121	0·050
Phosphoric acid .....	0·075	trace	trace
Silica .....	10·447	1·171	0·453
Silicate of lime .....	3·346	....	...
Organic matter .....	trace	trace	trace
Soluble salts .....	trace	trace	trace
Water and loss .....	9·446	2·578	1·757
	100·000	100·000	100·000

I. Substances separated by water from a muddy deposit taken from a discharge-channel.

II. Sinter from the Sprudelbecken.

III. Sinter taken from a discharge-channel in a dry state.\*

There are also great differences in the proportions of carbonate of lime and hydrated peroxide of iron contained in their deposits ; for those of the cold springs consist almost entirely of the latter, with mere traces of the former ; while the deposits of the hottest Carlsbad spring (166° F.) contains the largest quantity of carbonate of lime.

Among the numerous hot springs of Italy which deposit calcareous sinter, those of San Phillip, upon Monte Amiata, in Tuscany, deserve especial notice. The springs have there formed an entire hill of pure snow-white calcareous sinter, and the water flowing down is employed to make bas-reliefs, which can be done in the course of a few days. The sulphuretted spring solfatar, near Tivoli, rich in lime, is also famous in this respect.†

presence of oxides of copper and lead, Fresenius has still some doubt whether they are really to be ascribed to the springs, inasmuch as there is a brass cock supposed to be soldered with lead, not far from the spot from which the deposit III. was taken.

\* Fresenius, *Untersuchung der Mineralwasser in Herzogthum. Nassau*, 1850.

† Hoffmann, *Physikalische Geographie*. Vol. 1, p. 482.

In the Berberei, near Mjer-Ammar, between Bona and Constantine, a great quantity of hot water bubbles out, which has formed several conical hills of snow-white calcareous sinter. Most of these hills are only 5 or 6 feet, some 15 or 18 feet, in height.\* Between Ezerum and Trapezunt, at the northern foot of the Taurus, a warm spring, issuing from the side of the limestone rocks, with a strong evolution of carbonic acid, has built a wide arched bridge of tufa and stalactites over a river which pursues its way unhindered beneath. This natural bridge is now covered with earth and plants. Further down is a similar bridge half formed.† The nature of such building springs explains many ancient traditions in regard to rivers which build bridges of themselves, and are said to have petrified whole towns and all their inhabitants.

Asia Minor is rich in hot and incrusting springs. W. S. Hamilton mentions one between Smyrna and Brussah which deposits stalactitic and stalagmitic concretions, diffusing at the same time an odour of sulphuretted hydrogen. Hitchcock‡ has made some communications with regard to sediments formed by springs in Persia. He says, "that with the exception, perhaps, of a deposit of travertin around Rome, resembling statuary marble, he is not aware of any case besides those around the Lake Oroomiah in which the most beautiful marble is produced by springs. The Talreez marble is usually of a yellowish or light blue colour, perfectly compact, and so translucent that it is used in thin slices for windows of baths and other places. It occurs not far from Maraga, on the east side of Lake Oroomiah. Immense quantities of this marble have been dug and carried away. The common opinion is that the springs now deposit it, but one or two facts have led him to suspect this may not be the case. Above the marble there lies a deposit, several feet thick, of common tufa or travertin. Now Hitchcock suspects that this tufa is all the deposit which has been formed since the springs assumed their present state; and that the marble was deposited when their temperature was higher, and when perhaps they were beneath deep waters."

It is of interest to know that mineral springs can deposit granular limestone. I doubt whether hot springs are better suited to this than cold, from which the deposition takes place slower than from the former; but the slower the carbonate of lime is

\* Sedillot, in the *Compt. rend.* Vol. 5, p. 555.

† Eli Smith, in the supplementary volume to Poggendorff's *Annal.* Vol. 1, p. 374.

‡ Reports of the Meetings of the Association of American Geologists and Naturalists. Boston, 1843, p. 414.

deposited, the more likely is it to assume a crystalline form. A slight change in the constituents of the springs, besides the carbonate of lime, may very possibly have caused the difference between the earlier and latter deposits.

*Deposits of Carbonate of Lime from Cold Springs.*

These deposits are so frequent that it would be tedious to name the number of individual localities where they occur. Every cavity in limestone rocks where there are stalactites may be taken as an example, at least, of the deposition of carbonate of lime from water, which, filtering through fissures and crevices of the rock, dissolves carbonate of lime by the aid of the free carbonic acid which it contains, and again deposits it in hollow cavities in consequence of gradual and entire evaporation of water and escape of carbonic acid.

An extended layer of calcareous tufa in the basin of Canstadt, which was more closely examined by Walchner,\* shows, among others, what considerable formations springs are capable of producing. Even at the present time nearly 50 springs flow in the neighbourhood of Canstadt, of a temperature ranging from 66° to 70° F., which continually deposit tufa which is quite identical with that formed at an earlier period. Their quantity of water amounts in 24 hours to 800,000 cubic feet, from which, according to Walchner's calculation, a mass of stone weighing 200,000 pounds could be deposited.†

Those parts of Germany rich in limestone afford many examples of deposits of calcareous tufa; thus, the country between the Hartz and the Thüringer Wald, upon the Eichsfeld, near Langensalza, Mühlhausen, Gotha, Tonna. They are still formed so abundantly that in many places, as near Göttingen, it is necessary to clear out the mill channels through which such springs pass. Remarkable deposits of this kind occur at Königslutter, near Brunswick, and in the Trieb valley, near Meissen.‡ In a side valley which opens into the Weser, near Vlotho, I also found a very considerable layer of calcareous tufa, which has been excavated in some places to a depth of 12 or 15 feet without reaching its bottom. The calcareous sinter which was deposited in the Roman aqueducts, extending from the heights of the Eifel to Cologne and Trier, occurs in such large masses that columns were

\* Darstellung der geognost. Verhältnisse der Mineralquellen am Schwarzwalde, p. 35.

† It must be supposed, that this is the quantity of carbonate of lime which is annually deposited.

‡ Hoffmann, loc. cit., p. 481.

made from it, which are found here and there in the churches of the Eifel. According to my analysis, this sinter is a very pure carbonate of lime, for it consists of

Carbonate of lime...	...	...	99·35
„          magnesia	...	...	1·20
Peroxide of iron	...	...	0·13
			<hr/>
			100·68

Probably no country possesses so many remarkable deposits of sinter as Italy, where the immense chain of the Apennines, abounding in limestone, present an excellent opportunity for their formation. The travertine, lapis tiburtinus of the ancients, which the Romans used in the construction of their principal buildings, such as the Colosseum, and which is still being formed in the Campagno di Roma, has been famous from the remotest times. Its formation is, under ordinary circumstances, nowhere more abundant than at the cascade of Tivoli. There, small carvings, such as crucifixes, &c., are exposed to the spray of the water, and after some time they are covered with glittering granules of calcareous tufa.\*

The petrifying spring of Pambuk Kalessi† rises from a pond south-east of Smyrna, not far from the ruins of the ancient Hierapolis. Its largest waterfall rushes through the midst of groups of stalactites which it has itself formed into the valley beneath. Here snow-white stalactites, having a woolly appearance, arch over the stream like drooping bushes of weeping willow.

The following results may be deduced from the comparison of the analyses of calcareous sinter. The principal constituent of all these deposits from hot springs is carbonate of lime. If the springs contain carbonate of strontia, fluoride of calcium, and phosphates, they are always deposited with the carbonate of lime. The deposition of these substances depends solely upon the escape of the half-combined carbonic acid. It has already been pointed out why carbonate of magnesia so rarely occurs in these deposits. As the sprudelstone of Carlsbad contains no carbonate of magnesia, the entire quantity is carried away by the discharging water.

#### *Deposits of Gypsum.*

It would be as tedious as useless to bring forward examples of these deposits, which are formed wherever water containing

\* Hoffmann, loc. cit. p. 481.

† Supplementary volume to Poggend. Annal. Vol. 1, p. 373.



sulphate of lime in solution evaporates. For this reason crystals of gypsum are frequently met with in beds of clay under vegetable mould, in marl, gravel, as sand in plains along the seashore (Granada).\*

*Deposits of Hydrated Peroxide of Iron and of Protocarbonate of Iron from cold Carbonated Springs.*

About 20 years ago, I published a paper† upon the very considerable beds of ochre deposited and still being deposited by the numerous ferruginous carbonated springs in the valleys surrounding the Lake of Laach. These beds are in some places so extensive that they are sources of considerable profit.

The principal constituent of these deposits is hydrated peroxide of iron. One, which was very near the spring, was found to consist of

Peroxide of iron ... ..	80·64
Carbonate of lime ... ..	13·06
Silicic acid ... ..	6·30
	<hr/>
	100·00

The oxidation of the iron is therefore more active in causing the separation of the iron, than the escape of carbonic acid in causing the separation of the carbonate of lime. If both causes produced equal effects, there would be separated with every 80·64 parts of peroxide of iron 428 parts of carbonate of lime, or nearly 33 times as much as is really separated; for that is the proportion between the oxide of iron and the carbonate of lime in this mineral water. The silicic acid presents a similar behaviour. If this had separated with the peroxide of iron in the same proportion as they exist in the water, there would have been for every 80·64 parts of oxide of iron 39·4 silicic acid, or 6 times as much as is really deposited. The mineral water therefore carries away, after the deposition of the iron ochre, 33 times as much carbonate of lime, and 6 times as much silicic acid, as it actually deposits.

The ochreous deposit of another spring which I examined did not effervesce when dipped into acid, thus showing that it contained no carbonate of lime; but there was a trace of magnesia probably combined with silicic acid.

The same relations are therefore present in cold springs that

\* The deposition of gypsum in salt lakes, and in the sea, will be treated of in Chapter XVIII.

† Schweigger's Journ. Vol. 68, p. 420.

we have previously become acquainted with (p. 146), with the difference only, that the carbonate of lime is deposited much later from them than from the hot springs, from which the half-combined carbonic acid escapes much more quickly. It is on this account that the deposits of carbonate of lime from cold springs, when the discharged water stagnates or trickles slowly down the walls of fissures, are still freer from iron than those from hot springs; for the greater time which elapses before the deposition of the carbonate of lime, the more will the proto-carbonate of iron have separated as hydrated peroxide. But silica may be deposited simultaneously with the carbonate of lime.

Silica always separates sooner than carbonate of lime in drusy cavities; for the siliceous formations in them are the older, and the calcspar the newer. It is true that this order of succession is sometimes inverted, so that previously formed calcspar is again removed by water and a siliceous formation is introduced in its place, whence arise pseudomorphous minerals in forms of calcspar.

I have observed\* that at a certain depth under the ochereous deposit near Wehr, there is a bed of protocarbonate of iron, which is nearly white, but exposed to the air, it soon becomes dirty green. I endeavoured to explain the deposition of this carbonate, from the circumstance that the ochre beds generally rise more or less above the level of the mineral springs, and form small hillocks. If, for instance, the deposition continued after the formation of an ochre layer at the cost of the atmospheric oxygen, this layer would be forced upwards. So long as this deposition goes on under the influence of the air, iron ochre is formed, but if this has become so dense as to form an air-tight covering, hydrated peroxide of iron cannot be deposited any longer. A further deposition of iron can only take place in the same way as the calcareous sinter, by the gradual escape of a part of the carbonic acid, in consequence of which the iron is separated as carbonate. This action is especially favoured by the circumstance that, by the first deposition of ochre, the discharge of the spring is contracted and a partial stagnation of the water results. A bog is thus formed round the spring, the water spreads out, and its evaporation and the escape of the carbonic acid are hastened by the increased surface. As the subsequent depositions of carbonate of iron take place between the crust of hydrated peroxide and the original surface, it is evident that the whole deposit must rise upwards until such time

\* Loc. cit.

as the pressure of the mass deposited becomes so great that the water is forced to seek another discharge where there is less obstruction.

I also remarked that other special circumstances must obtain in the deposition of carbonate of iron, because it is not always found under the iron ochre. It frequently happens that where the most considerable beds of ochre are met with, there are no longer any mineral springs. There can be no doubt, in such cases, that they have become stopped up, and have sought an exit at some lower point as is not unfrequently seen. If the formation of ochre had advanced so far that the subsequent deposition would not be influenced by the air, and the further action of the spring then ceased, there could be no deposition of protocarbonate of iron such as otherwise would occur. It may be on this account that no carbonate of iron is met with under most beds of ochre.

I obtained some further elucidation of the formation of this carbonate on the opening of a mineral spring in the Brohl valley. I found, for instance, sphærosiderite at a depth of 9 feet, which consisted of 77·3 parts carbonate of iron, 2·6 carbonate of lime and earthy admixtures, especially pulverized volcanic tufa\* (trass).

\* On opening this spring, a bed of iron ochre was found 3 feet in thickness. Under this was a bed of clay 6 feet thick, which contained, at its surface of contact with the former roots, stems of grass and pieces of wood. Beneath the clay was a crust of sphærosiderite,  $\frac{3}{4}$  of a foot thick, and under it trass, which was so softened by the mineral water that it could be broken through with the spade. The trass had not its ordinary consistence for a foot beneath the sphærosiderite. This latter is, without doubt, a deposit from the mineral water. The carbonic acid was probably derived from the alkalies and alkaline earths of the trass, and the proto-carbonate of iron held in solution by it deposited as sphærosiderite, while the resulting alkaline and earthy carbonates were carried away by water.

This spring also presents an example of how ferruginous springs become stopped up by their ochreous deposit, and then seek a discharge at a lower point. In making this excavation, there was found 2 feet under the ochre bed, and 5 feet under the surface, a quantity of bricks. Several were fragments of a cornice, others hollow, as if they had been part of a conducting tube, and others again were flat and thicker than ordinary tiles. Large blocks of grauwacke and basalt were interposed. It is probable that these stones were all remains of a previous enclosure of a spring, and perhaps of a bath-house. Under these remains, which decidedly belong to the time of the Romans, fragments of an earthen urn were found, also a flat vessel ornamented with figures, fragments of a bone and of rusted shears. Under the stones were fragments of a Roman altar of trass, such as those found in the Brohl valley. A much larger altar-stone, slightly ornamented, lay sideways upon a spot where there was a strong evolution of carbonic acid. Finally, under all these, there were found upon the crust of sphærosiderite where a vein of the spring issued, seven copper coins, with figures of J. Cæsar, Augustus, Tiberius, Vespasian, &c., lying quite close to each other. A silver coin was subsequently found in the excavated earth.

The Romans had undoubtedly sunk through the clay, and erected their building upon the sphærosiderite. After its destruction, the clay may have been thrown over the remains from all sides, together with the large blocks of stone.

The small quantity of carbonate of lime in proportion to carbonate of iron in this sphærosiderite is worthy of notice. The analysis of the carbonated spring from which this sphærosiderite had been deposited, showed that the carbonate of lime amounted to nearly 4 times as much as the carbonate of iron, while in the deposit, on the contrary, the latter is 30 times as much as the former.

I have showed by calculation what considerable quantities of iron ochre are still being deposited in that district by the active mineral springs, according to which they are capable of forming in 1000 years a bed 3 square miles in extent and one foot thickness. One mineral spring yielded in a year 2,628 pounds of hydrated peroxide of iron, a quantity which would fill a fissure of 2 inches width, 2,566 feet long, and as many deep.

The above-mentioned circumstance, that the existing mineral springs rise at a lower level than the beds of ochre, is very frequently observed in that district. The denudation of the valleys may also have contributed to cause this, besides the above-mentioned cause, as the springs generally occur in the deepest parts of the valleys. Deposits which had previously been formed upon brooks, are naturally carried away by this denudation.

It may also be observed in this country, that the deposits of earlier times were of a different character from those of the present time. At higher levels than the present deposits, considerable beds of calcareous sinter are met with in some places, while the present springs form only beds of ochre with slight admixture of carbonate of lime. It is, however, possible that this calcareous sinter was formed by springs which had deposited iron ochre at previous parts of their course, and carbonate of lime at subsequent ones.

The inverse case, that springs have now a higher discharge than formerly, also occurs. There are, for instance, beds of calcareous sinter here and there, covered with considerable beds of iron ochre. It may be, that in this case springs which had flowed for a long distance and deposited carbonate of lime, ceased to flow, or

But the bed of ochre, three feet thick, was formed since the time of the Romans, for it was not altered in its position in any place, and there were likewise no stones in it. The bricks and pieces of grauwacke, which were near the bed, were covered with a hard crust of iron ochre. In the ochre-bed itself there were also hardened druses of brown iron ore.

This re-discovered mineral spring had, therefore, pursued its course for a period of many thousand years between the trass and the clay, and deposited there the crust of sphærosiderite.



changed their course, and that other springs broke out near these calcareous beds, and flowing over them, deposited iron ochre upon them. The deposits of iron ochre and carbonate of lime, formed by springs whose points of discharge are far distant, explain the very varied modifications in the relations of stratification of the two deposits.

Deposits from cold springs recently analyzed, very strikingly show the minute quantity of carbonates deposited by their waters.

	I.	II.	III.	IV.	V.	VI.
Peroxide of iron....	57.30	65.30	53.88	40.57	50.42	53.10
Sesquioxide of manganese ..	..	0.76	6.95	trace	...	...
Lime .....	6.68	0.15	0.40	...	...	...
Magnesia .....	...	0.04	0.12	...	...	...
Protoxide of iron .....	...	...	1.68	...	...	...
Carbonate of lime .....	...	...	...	2.11	2.36	4.50
„        magnesia .....	...	...	...	1.06	0.83	0.67
Alumina ....	...	...	...	...	3.97	2.91
Sulphuric acid .....	0.54	...	...	...	...	...
Silica, soluble .....	...	0.43	6.91	5.00	2.00	4.20
Arsenic ....	...	0.96	0.025	0.05	0.03	0.06
Arsenious acid .....	0.06	...	...	...	...	...
Copper ....	...	0.017	0.001	trace	...	...
Tin .....	...	0.003				
Water .....	23.34	26.33	23.93	18.00	20.03	19.51
Organic matter .....	0.54			16.80	15.19	12.33
Sand .....	5.39	6.02	6.71	16.41	3.97	2.72
Carbonic acid ....	6.15	...	1.36	...	...	...
Loss ....		...	...	...	1.20	...
	100.00	100.1	100.966	100.00	100.00	100.00

I. From the acidulous spring at Driburg.\*

II. and III. From the Bade and Trinkquelle of Alexisbad, upon the Hartz, &c.†

IV. From a spring at Foix.

V. From a spring, St. Madeleine de Flourens.

VI. From a spring near Toulouse.‡

The analysis of the deposit from the channel, in which water is conducted from Arcueil to Paris, shows that the deposits from water which is not exposed to the air, are quite different from those which result when air is present. The deposit mentioned consists of

\* Ludwig, Archiv. der Pharmacie (2) Vol. 51, p. 145.

† Rammelsberg, Poggendorff's Annal. Vol. 72, p. 571.

‡ Filhol, Pharmac. Journ. (3) Vol. 13, p. 13. The deposits IV, V, and VI were dried at 212° F.

90 parts of carbonate of lime, 6·0 carbonate of magnesia, 2·2 sulphate of lime, and 1·8 silica, peroxide of iron, and organic matter.\*

Modifications and complete transformations in the deposits have undoubtedly taken place by the replacement or complete removal of constituents of the original deposits. If certain deposits had been formed by water, and their constituents subsequently altered, it might happen that what was previously deposited, was entirely or partially removed and other materials substituted for it. Thus pre-existing substances, formed in an entirely different manner, might entirely change their constituents by such an interchange when brought into contact with water. The following will serve as an example of such an interchange.

In a petrified human skull no trace of the original bony substance could be discovered, it appeared to be intermediate between earthy-brown coal and earthy-brown iron ore. By long distillation it yielded products similar to those of brown coal, and not a trace of ammonia. On analysis it was found to contain,†

Organic matter, resembling brown coal	....	....	46·15
Peroxides of iron and manganese, containing much phosphoric acid	....	....	41·90
Water	....	....	9·00
Earthy substances insoluble in acids, principally silica	....	....	2·40
Traces of sulphate of lime	....	....	....
			<hr/> 99·45

The whole of the lime of the carbonate and phosphate had therefore been removed by water and replaced by oxides of iron and manganese, which combined with the phosphoric acid. It may be, as Kersten conjectures, that it was sulphate of iron, resulting from iron pyrites, which effected this decomposition. It is striking that the organic matter amounts to 14 $\frac{0}{100}$  more than in bone.

#### *Deposits of Oxide of Manganese.*

Most of the deposits of iron ochre contain small quantities of peroxide of manganese, but deposits in which this substance is the principal constituent are not so frequent. During the repair of a water-channel hewn in the rock in the neighbourhood of Nürnberg, an immense mass of hydrated oxide of manganese was found.‡ A

\* Boutron—Charland and Henry. Ibid., Vol. 14, p. 173.

† Kersten, Archiv. für Mineralogie, &c. Vol. 16, p. 372.

‡ Leuchs, Journ. f. pract. Chem. Vol. 21, p. 399.

spring near the Cape of Good Hope, having a temperature of 110° F., is said to deposit in the discharge channel, a very thick incrustation of oxide of manganese, extending to some distance from the spring.\* Kersten found in a mineral spring (68° F.), in the house of the Russian Crown at Carlsbad,† a mass homogenous in some parts and resembling manganite. On solution in hydrochloric acid, it evolved chlorine. In an agate druse, in amygdaloid near Idar and Oberstein, which I opened myself, I found upon the amethyst crystals a dark-brown moist mass, consisting of peroxides of manganese and iron, and silicic acid, which gave off chlorine with hydrochloric acid.

The following deposits are especially worthy of notice :

	I.	II.
Oxide of manganese ....	35.0	25.01
Peroxide of iron ....	6.5	22.90
Baryta ....	4.5	...
Quartz-sand ....	50.0	Silicic acid 18.98
Alumina ....	4.0	...
Water ....	...	33.00
	100.00	100.00

I. Deposit from the springs of Luxeuil, which evolves chlorine with hydrochloric acid.‡

II. Deposit from mine-water in a mine at Freyberg which was still being formed.§

The presence of peroxide of manganese in the above deposits, shows that it may be produced from carbonate of manganese by atmospheric oxygen, after the deposition of the latter.

With regard to the occurrence of manganese ores in the Hunsrück, and in Soonwald upon the left bank of the Rhine, Nöggerath gives an account.|| They occur upon the tolerably high mountain ranges as well as upon the declivities. It may without difficulty be imagined, that water containing atmospheric carbonic acid, dissolves protoxides of iron and manganese and deposits them again while, running down fissures and planes of stratification.

\* Townsend, l'Institut. 1844. No. 529.

† Karstens' u. v. Dechen's Archiv. Vol. 19, p. 754.

‡ Braconnot, Ann. de Chim. et de Phys., Vol. 18, p. 221.

§ Kersten, loc. cit.

|| Kersten's u. v. Dechen's Archiv. für Mineral. &c. Vol. 16, p. 470.

It cannot be doubted that the water which formerly deposited silicic acid, and thus formed the quartz dykes which occur there, took the same course from above, downwards. The frequently large quantity of protoxides of iron, associated with small quantities of protocarbonate of manganese in the clay-slate, has, without doubt, afforded the material.\*

The deposits of ore occur where the clay-slate and the grau-wacke are very much decomposed, soft and bleached: a proof that their iron and manganese have been removed by the water.† Brown iron ore also occurs in the crevices of quartz, and sometimes psilomelan and pyrolusite.

The descending waters continue to dissolve protoxides of iron and other bases, so long as their carbonic acid suffices; when this is saturated, nothing more can be dissolved. But if they penetrate into deeper crevices or into the rock itself, they deposit the dissolved protoxide in consequence of the oxidizing action of the air present in the minutest crevices. The carbonic acid thus set free, is capable of dissolving fresh quantities of protoxide of iron, &c., and repeating the process. Thus, the minute quantities of carbonic acid which the fresh water carries with it, is capable of continually dissolving fresh quantities of these oxides, until finally the water escapes as springs, or flows into the water which communicates with that of rivers. The solution may therefore proceed from the surface of a rock to great depths.

### *Deposits of Sulphuret of Iron.*

The deposits of metallic sulphurets by springs are among the most remarkable, because they are formed from different constituents of them.

Longchamp‡ appears to have been the first who found iron pyrites as an undoubted deposit from mineral water in a narrow channel of the warm spring of Chaudesaigues in Cantal. He considered it, however, difficult to explain how it was formed there. Nöggerath§ made some interesting remarks on the subject at the thermal springs of Aix-la-Chapelle: namely, that in cleaning the

\* We shall afterwards see that organic substances in clay slate may also reduce the peroxide of iron to protoxide.

† It is affirmed that at great depths, where the clay-slate is harder, the deposits of iron-stone terminate. On the surface, where the rock is harder, they are entirely absent.

‡ Annal. de Chim. et de Phys., Vol. 32, p. 260.

§ Schweigg. Journ., Vol. 49, p. 260.



spring basin, fragments of transition lime-stone, between which and the grauwacke the spring issues, were found covered with a thin coating of iron pyrites.

Shortly afterwards (1831), I had an opportunity of making a similar observation at the enclosure of a mineral spring. As the hollow wooden tube, through which the spring previously issued, was taken away, and the loose earth removed, dark-yellow iron pyrites of a metallic lustre were found in it; they were seldom crystalline, and contained pieces of vegetable stalk or splinters of wood, which appear to have given the first occasion to its formation. It scratched glass plainly, and the analysis showed it to be pure iron pyrites. The water contained  $\frac{1}{33333}$  sulphate of soda.

I found the key to the explanation of this phenomenon by other experiments. In order to prevent the precipitation of iron in mineral waters, I filled a large number of bottles, and put into each a small quantity of sugar, closed them with cork, pitch, and leather, in the usual manner. After about 13 months, black flocks had separated, which were sulphuret of iron. After  $3\frac{1}{2}$  years, I opened several of these bottles. The contents of all of them smelt more or less strongly of sulphuretted hydrogen, and the same black powder had separated, and sometimes also black flocks. The analysis of this black powder, collected from more than 30 bottles, showed that it had nearly the composition of iron pyrites. It is worthy of notice, that it was mixed with  $50\cdot4\%$  of silica, which remained behind, of a black colour, after the treatment of the whole with nitro-hydrochloric acid; but on heating in the air, it lost  $13\frac{0}{6}\%$  in weight, and became white.

The mineral water itself was scarcely clouded by chloride of barium after separation of the black powder. The sulphate of soda which, in the unaltered water, amounted to  $\frac{1}{100000}$ , had therefore been decomposed by the sugar. The sulphur had yielded one constituent, and the iron of the carbonate the other. The formation of iron pyrites at the cost of sulphate of soda and carbonate of iron was therefore proved, as well as the possibility that such a change might take place wherever sulphates, protoxides of iron, and organic substances, came into contact in the presence of water.\* The law above-mentioned (Chapt. I., No. 27.) was in this way discovered.

\* Further examples of the formation of iron pyrites in this manner, are given in the German edition, Vol. 1, p. 919.

*Deposits of Sulphuret of Zinc.*

Twenty years since\* there was found in a lead-mine, east of the Siebengebirge, upon old mine-timber, a sinter of nearly two lines in thickness, which separated in thin scales, and sometimes contained between them, or beneath the sinter, an extremely delicate coating of sulphur. The fracture showed no trace of crystalline structure, the sinter was of an opaque light pea-yellow or ashy grey colour. According to my analysis of the purest pieces, it consisted of:—

Sulphuret of zinc	....	....	37.571	} Soluble in nitric acid.
"      cadmium	....	....	0.279	
Sulphur	....	....	0.241	
Peroxide of iron	....	....	1.392	
Silica	....	....	28.886	} Insoluble in acids.
Alumina	....	....	9.424	
Peroxide of iron	....	....	3.023	
Lime	....	....	0.410	
Magnesia and organic matter	....	....	4.576	
Water and volatile constituents	....	....	14.198	
			<hr/> 100.000	

It cannot be in the least doubted that this sinter was deposited by water which came in contact with the mine timber. According to historical records, this formation may have begun between the 12th and 15th centuries; however, it probably first took place most considerably when the galleries became choked up, and thus were either entirely or partially filled with water.

With regard to the deposition of sulphuret of zinc and cadmium, two assumptions are admissible, which, however, both presuppose the oxidation of blende in the mine, and the solution of the sulphate of zinc—a circumstance which frequently occurs in other places. Either sulphuretted hydrogen, which is so abundantly and frequently developed by decomposition of old wood-work in abandoned mines, came into contact with the solution of sulphate of zinc and precipitated the sulphuret, or this solution was decomposed by the wood, upon which the sinter was deposited, as sulphate of iron is decomposed by organic substances. Whether the iron which is dissolved by the nitric acid, had also been deposited as iron pyrites or as hydrated peroxide of iron, cannot be determined. The small excess of free sulphur might favour the first view, as it may result from decomposed iron pyrites. The iron in the silicate

\* Nöggerath and G. Bischof. Schweigger's Journ. Vol. 65, p. 245, &c.

could have existed only in an oxidized state, probably as protoxide.

The sinter in question shows decisively the possibility of the formation of sulphuret of zinc by aqueous agency. Besides silicates which the water held in solution, there was a salt of oxide of zinc.\*

*Deposits of Calamine from Water.*

Nöggerath† found in old mines at Tarnowitz, in Upper Silesia, the timbering and bundles of leaves covered with crusts of carbonate of zinc. As this mode of occurrence decidedly proves the deposition from water, it may be inferred that the beds of calamine in Upper Silesia and Poland have been formed in the same manner. According to V. Monheim,‡ there are, in the mine of the Busbacher Berg, near Stolberg, places in which the walls, consisting of brown iron ore, are covered with a crust of white zinc-spar. One of these places has been worked probably for 200 years, the other for 60 years. The zinc-spar has, therefore, been deposited in this period. When these workings were again opened in 1846, the galleries were found full of carbonic acid; there was, therefore, no want of solvent for the carbonate of zinc. In the hard calamine of Herrenberg, near Nirm, there were likewise found pieces of wood. The process of solution, therefore, goes on in the mines of Silesia as well as those of Busbach, and it is in the surrounding rocks that the carbonate of zinc is to be sought, for where it existed, and still exists, Karsten§ found in four dolomites, mostly from the Scharlei mine, near Tarnowitz, or near it, carbonate of iron and carbonate of zinc 1·2 to 1·75%, and in one only, carbonate of zinc 0·5%. Monheim found, in compact dolomite from the borders of the calamine-beds of Altenberg, near Aix-la-Chapelle, 1·38%, and Davreux, in dolomite from Membach, near Eupen, 9·75%.|| In a kind of dolomite from Tunis, Berthier found¶ as much as 28·9%, and 3 to 19% carbonate of lead, the latter also in some zinc-spars. Bergemann has informed me that he found from 0·5 to 19·2% carbonate of zinc in 17 different dolomites from Westphalia.

\* The conversion of zincked iron into artificial blende in impure sea-water is worthy of remark. R. Mallet, in London Journ. of Arts, 1844, Feb., p. 44.

† According to a letter from Tarnowitz, Nov. 17, 1843.

‡ Verhandl. des naturhist. Vereins, der Preussischen Rheinlande. 1845, p. 75; 1848, pp. 36, 39, 41, 157, 162, 171; 1849, pp. 1, 24, 49, 54, and official report upon the assembly of German Naturalists in Aix-la-Chapelle.

§ See his Archiv. für Mineralogie, &c. Vol. 17, p. 57.

|| Verhandlungen. 1845, p. 76.

¶ Ibid., p. 77.

*Deposits of Bog-iron Ore from Water.*

The several varieties of this ore are sediments which have been formed partly by chemical, and partly by organic action.

Kindler\* made the following observation as to the formation of this ore: On the declivities of sand-hills planted with pine trees, and where springs lying lower down cause falls of earth, dead roots which penetrate through the ferruginous quartz sand absorb the rain-water filtering through. A decomposition commences, by which acids are formed, which are capable of dissolving large quantities of protoxide or peroxide of iron; for in a few months the sand becomes as white as if it had been treated with acid. The action of a root, two lines in thickness, extends to a distance of from one to two inches. This phenomenon also presents itself in woods and gardens: decolorized sand is found everywhere under rotting leaves. Daubree† observed this decolourization of ferruginous sand by roots, in large extents in the plain of the Rhine and Lorraine. If a decaying root and quartz sand, coloured with oxide of iron, are often moistened with water, it will be found ferruginous, after filtering and evaporating. This process of decay acts, therefore, as a powerful deoxidizing agent.

During the decay of vegetable substances, there are formed carbonic acid, crenic acid, &c.‡ Protoxide of iron is dissolved in both acids, the combination of crenic acid with peroxide of iron is insoluble in water, but soluble in ammonia. If, therefore, there are decaying nitrogenous substances present which evolve ammonia, this salt may also be dissolved. The apocrenic acid behaves towards the oxides of iron in the same way as the crenic acid. The humic acid occurring in vegetable mould, also gives a compound with peroxide of iron which dissolves in 2,300 parts of water.

In marshes and morasses there is, then, no want of acids which are capable of dissolving protoxide and peroxide of iron, and Kindler's observations show that such solution really does take place. If, by the decay of vegetable and animal substances, phosphates, especially phosphate of lime, are separated, which dissolve in carbonated water, the conditions for the formation of phosphates of protoxide and peroxide of iron are complete. It must nevertheless be remarked, that analysis has not hitherto shown the presence of lime in

\* Poggend. Annal. Vol. 37, p. 203.

† Comptes rendus. Vol. 20.

‡ Apocrenic acid (1 to 2.5 per cent.) has been found by Hermann in a bog-iron ore from Nischne Nowgorod in Russia.



bog-iron ore. In so far as phosphate of lime has yielded the phosphoric acid, the resulting carbonate must have been removed by water. Phosphate of iron may also originate in already-formed proto-carbonate of iron, when phosphate of lime is separated by the decay of organic substances. (Chapt. I, No. 20.)\*

A careful observation of the marshes shows the following process:—The water in them is iridescent upon the surface; it forms a thin film: this is the opposite of the deoxidation process; namely, the gradual oxidation of protocarbonate of iron. It is the same phenomenon that is observed when this carbonate is prepared from iron-filings and water, through which carbonic acid is passed. If this solution, at first perfectly clear, is exposed to the air, it becomes covered with an iridescent film, and after a little while peroxide is precipitated.

The carbonate of iron present in the water of marshes, originates from supplies containing it in solution, or from peroxide of iron contained in suspended matter, which is carried by water, and deposited upon the bottom of the marshes, where it is deoxidized in contact with organic remains. The hydrated peroxide of iron which is formed by oxidation of the carbonate of iron, and falls down, suffers the same reduction. But when the organic remains at the bottom of marshes have been completely destroyed by the process of decay, the reduction of the precipitated peroxide of iron can no longer go on, and then beds of bog iron are formed. All the peroxide of iron disseminated throughout the rocks and earths, within the range of the process of decay, will be also deoxidized, and converted into soluble carbonate of iron, which is again precipitated by oxidation.

In these processes the protoxide of iron acts the part of a carrier to the oxygen, transferring it to the decaying substances at the bottom of marshes, and which, in consequence of the covering of water, does not come into immediate contact with the atmosphere. It is, therefore, obvious that the decomposition of organic matter in places where the oxygen is carried to it by peroxide of iron, goes on more rapidly than in other places where only the oxygen absorbed by the water of marshes comes in contact with organic matter. Here, as in every other instance, nature works productively, at the same time as destructively. Organized matter is broken up, and mineral formations supply their place. The

\* It has been long known that, in the government of Olonetz, the iron ore deposited in marshes contains more of phosphoric acid than that which is deposited in lakes. *Annuaire des Mines de Russie*. 1835, p. 240.

peroxide of iron disseminated throughout rocks and earths, and in that state useless to us, is extracted and collected in deposits which are profitable for districts in which other and better iron ores are wanting.

This process of deoxidation of peroxide of iron goes on also in vegetable earth; for Richard Phillips, Jun., and Wilson,\* found that the iron contained in the soils analyzed by them, was principally in the state of protoxide. The quantity found in five of the most productive kinds of soil from England, Belgium, and India, varied between 3 and 14%. The protocarbonate of iron produced in the soil by the deoxidation of peroxide, at the cost of humus, and combination with the carbonic acid, thus formed, is preserved against the oxidizing action of the atmosphere by the humus.

It may easily be seen that the reduction must proceed more rapidly than the formation of carbonate of iron, even if the former was effected only by the carbon of the organic matter, and not at all by the hydrogen; for 2 equivalents of peroxide of iron yield, in their reduction to protoxide, only one equivalent of carbonic acid, and this saturates 1 equivalent of protoxide, while 4 equivalents are formed. Therefore, even in this case, only  $\frac{1}{4}$  of the protoxide formed is converted by the simultaneously formed carbonic acid into carbonate;  $\frac{3}{4}$  remain; and if, as there is no reason to doubt, the hydrogen of the organic substance also takes part in the deoxidation of the peroxide,—if, therefore, besides carbonic acid, water is formed, the quantity of protoxide remaining as such, must be still more than triple that which combines with the simultaneously formed carbonic acid. However, if the water in which this decomposition is going on, takes up carbonic acid from the atmosphere, all protoxide of iron formed may be converted into carbonate.

We cannot but assume, that the silicate of protoxide of iron present in sedimentary formations may be formed by reduction at the cost of organic substances; for the suspended matter carried to the sea or lakes, contains for the most part silicate of peroxide of iron. This reduction may be easily conceived, for organic matter is abundant in these waters.

Ehrenberg† found by the aid of the microscope, in the yellow ochre, which occurs in very voluminous masses in marshes and turf plains, extremely delicate branched threads, the branches

\* Phil. Mag. Vol. 26, No. 174.

† Poggendorff's Annal. Vol. 38, p. 217.

being only  $\frac{1}{1000}$  of a line in thickness; they had a yellow colour. These delicate threads do not lose their form by strong ignition, but assume the reddish-brown colour of the ignited iron ochre. There is, therefore, an organized body closely resembling the Gaillonella of the Bacillaria, but very small, which contains an extremely large quantity of iron. The same were observed in different kinds of bog-iron ore, from the district of Berlin, the Ural, New York, &c. The ochreous deposits of salt brine (from Colberg and Dürrenberg) likewise contain such infusoria, which closely resemble the Gaillonella ferruginea. While living they appear to be always yellow, but when dead to collect towards the surface and assume a greyish green colour, which changes to yellow upon their sinking again.\*

It might be inferred from this, that the skeleton of these infusoria consists of hydrated peroxide of iron, but that after their death it is reduced to protoxide by the reducing action of the decaying organic matter, and then again oxidized by the atmosphere. This would be in correspondence with what has been previously mentioned. But as the hydrated peroxide of iron in marsh-water is first formed from the dissolved carbonate of iron, the suspended, and not the dissolved iron, must yield the material for the shells. Perhaps the assimilation of the iron in solution, and its oxidation to peroxide, is one and the same act, It is, at least, difficult to conceive how solid bodies could be assimilated as such by these microscopic animals.

According to Ehrenberg, the infusoria of the bog-iron ore are only  $\frac{1}{1000}$  of a line in diameter, or  $\frac{1}{2}$  the thickness of a human hair. A cubic line of such animals would consequently contain 1000 million of such living organisms. The presence of silica in bog-iron ore, and the incombustible organic structure of the very small corpuscles, which form the surrounding ochre, make it very probable, as Ehrenberg remarks, that here also an organic relation by infusorial formation comes into play, so that these animalcules after their death form a nucleus towards which the dissolved iron immediately around is attracted.

We can only consider the development of the infusoria as a phenomenon co-ordinate with the formation of bog-iron ore; for, as was previously shown, the decay of organic substance going on in marshes is quite sufficient to explain this formation.

It will be seen from the above consideration, that the bog-iron ore is, next to the iron ochre, &c., deposited from mineral springs.

\* Several analogous phenomena are mentioned in Bronn's Handb. einer Geschichte der Natur. Vol. 2, pp. 405 and 406.

This is one of the most recent formations of iron ore, and indeed of those which are still going on, and is of very frequent occurrence.

Daubree\* directs attention to the fact of the occurrence of these beds of iron ore in the neighbourhood of slowly-flowing rivers, the Elbe, the Oder, the Spree, the Neisse, &c., which are connected with marshy lakes, or with lakes which are supplied by rivers. More than a thousand of such lakes in Sweden, Norway, Finland, and northern Russia, afford examples of this.

This ore is seldom more than 3 feet below the surface; it is covered with sand or mud, and very frequently with turf; its thickness seldom exceeds 2 or 3 feet, and is generally much less. The ore from the lakes frequently occurs in isolated spheroidal granules, with a concentric structure which sometimes resembles the roggens of the tertiary formation. It is also met with in the form of small shingles of  $\frac{1}{3}$  of an inch in diameter.

The deposits of iron ore are carried to the neighbouring brooks and rivers at high water. So long as these flow rapidly, nothing is deposited, but where their velocity is considerably lessened, especially in stagnant pools which are at a short distance from the banks, the suspended peroxide, or even dissolved carbonate of iron, is deposited. As the deposit penetrates on both sides into the sand, it separates in the form of veins and nodules.

If the rivers form lakes in consequence of considerable widening, as in Scandinavia and Finland, the greater part of the hydrated peroxide of iron is deposited by the stagnant water. The excess is carried away by the river, and the same phenomenon is repeated along its banks wherever marshes are formed. The remainder finally reaches the sea, where the peroxide separating, undoubtedly serves as a cementing material for other loose deposits.

It is evident that the formation of this ore of iron must have taken place during all the earlier sedimentary periods since the appearance of vegetation upon the earth. To this epoch belong the ferruginous veins and nodules frequently distributed throughout the diluvial sand and gravel. It is especially worthy of notice, that the two sedimentary formations, brown coal and coal, which contain the largest quantity of vegetable remains, are in general the richest in iron ores. Sphærosiderite and brown iron ore are frequently found in the latter: compact and sometimes argillaceous carbonate of iron, in thin beds or in flattened nodules, often occur in large quantities, as in the coal formations of England and Scotland.

\* Loc. cit.



The frequently considerable quantity of protoxide of iron in slate clay, shows that it can still yield materials for the formation of such iron ores.\* In the formation of carbonate of iron from this rock, there is the additional circumstance to be considered, that, besides the carbonic acid formed by the reduction of the peroxide of iron, carbonic acid and carburetted hydrogen are also evolved by the gradual transformation of the vegetable substances into coal. These gases penetrate the slate clay beds over the coal, the carburetted hydrogen acts as a reducing agent, and the carbonic acid combines with the protoxide of iron formed.

*Deposits formed in the Sea by organic action.*

It is an indisputable fact that the low islands in the ocean are nothing else, at least in that part of them which is visible, than the wonderful work of the coral animals, hence the name of *coral islands*. But a great variety of shells, and among them some of the largest and heaviest of known species, also contribute to augment the mass. Although only a peculiarity of the Indian and Pacific Oceans, still the immense area which the coral islands occupy is scarcely to be estimated. The coral-reef west of New Caledonia extends for a distance of 400 miles, and the great Australian reef has a length of 1000 miles. Millions of men dwell upon the decayed calcareous skeletons of these animals. Even if the masses which the coral animals build up, do not upon the average exceed 25 to 30 feet in thickness, still Captain Belcher bored a coral island to a depth of 45 feet without penetrating through the coral mass. Darwin does not doubt but that under favourable circumstances these animals can build up masses of considerable height, one above another, as is shown by columns and annular reefs of some coral islands, with perpendicular walls having a depth of 300 feet.†

Attempts have been made to compare such strata (which are imposing, less from their thickness than from their extension, and

\* It is worthy of notice, that H. Taylor (Edinb. New Phil. Journ., Vol. 2, p. 140) found in a bituminous slate-clay, from the Hartley colliery, near Newcastle, which contained 39·4 per cent. of carbonaceous substance, 4·3 per cent. of protoxide of iron; in a bluish slate-clay, which formed the roof of this stratum, and contained no carbonaceous substance, 4·5 per cent. protoxide, and 4·6 per cent. peroxide of iron. In the former case, all the peroxide had been reduced; in the latter, it is probable that a small quantity of previously existing carbonaceous substance had been consumed in the reduction, which could not further advance, on account of the want of deoxidising substances. The bluish slate-clay contains many nests of iron-stone. Kremers (Poggend. Annal. Vol. 84, p. 72) found in a slate-clay 11 per cent. of protoxide of iron.

† Poggend. Annal. Vol. 64, p. 563, et seq.

consisting as they do mostly of carbonate of lime), with the carbonate of lime occurring in sea-water. Surprise is expressed that sea-water is found to contain scarcely  $\frac{1}{100000}$  of this substance (p. 109), consequently scarcely  $\frac{1}{10}$  of that which water is capable of dissolving. It is not to be imagined how a substance can separate from a solution so far removed from the point of saturation, without a considerable evaporation taking place. However, as his separation goes on before our eyes in the coral-banks and in the innumerable testacea, the question arises how is it effected?

Nowhere does the important influence of the organic kingdom appear in a more wonderful manner than in the separation of lime from the sea. The numberless marine animals which have calcareous skeletons, partly internal and partly external, are the means of maintaining the equilibrium of the carbonate of lime dissolved in sea water, and marine plants also contribute towards it.

Could it be doubted that the coral animals form their skeletons only from the carbonate of lime dissolved in sea-water, the observation of Ehrenberg,\* that he never saw corals grow where the sea was frequently rendered turbid by shifting sand, but only where it is clear and pure, would entirely remove this doubt. Numerous observations of earlier navigators, as well as the later ones of Darwin,† have proved the same. The latter describes a coral-bank on the west of Mauritius, which surrounds this island, and which, although in general continuous and tolerably well bounded, is always interrupted at places opposite where a river falls into the sea. He considers this as an evident consequence of the turbid or impure water destitute of salt, which the river discharges into this sea, and which the zoophytes do not like. This is indisputably an important observation, since it gives a simple reason for interruptions in coral-reefs, whence further inferences may be drawn.

It may readily be conceived that, as a general rule, organic remains should be more frequent where limestone strata occur, if it is by vital agency that these have been produced. If also limestones occur which are nearly destitute of petrifications, we must not forget that Ehrenberg's investigations made us acquainted with microscopic animals which have in all probability effected the separation of the carbonate of lime of all the lime strata in which we are unable to detect petrifications with the naked eye. Consequently many, and perhaps all European chalk,

\* Poggend. Annal. Vol. 41, p. 269.

† Ibid. Vol. 64, p. 572.

consist of the remains of microscopic coral animals with calcareous shells, and of others with siliceous shells, from  $\frac{1}{24}$  to  $\frac{1}{2\frac{1}{8}}$  of a line in magnitude.\*

The thickness and extent of the chalk formation are sufficient to show the important influence of organic life upon the mineral formations in the sea. The traces of similar relations have been followed as far as the oolite limestone of Cracow, by Zeuschner, and even to mountain limestone of Russia, by V. Helmersen.†

According to Ehrenberg's‡ observations in the Red Sea, the living or dead coral animals never form beds one above another, but only a simple incrustation of most of the rocks under water. The height of the coral stratum often amounted to only 1 or 2 feet, and in no place, so far as it could be examined, to more than 10·5 feet, according to the magnitude of the separate blocks. Careful observation of the peculiar structure of the several forms of coral animals, shows clearly that all those which principally form strong masses, are altogether incapable of building up solid walls to protect themselves from the breakers, as Forster supposed. The coral animals do not live in strong tubes, or build, like wasps, a common protective house or nest. Neither are they, like oysters, protected by shell coverings; but, in all true corals, the soft parts are external, and the tree-like or globular skeleton forms the interior bones, or the lower pedicle. The tubiporous corals, indeed, with their mineral epidermis, live, as it were, in strong sheathings, but it is precisely these which do not live in the heaviest breakers, and are also more delicate and fragile than many others, as well as much smaller. The living corals in the Red Sea are not found at great depths. Ehrenberg could not find them at a depth of six fathoms, although the edges of the islands or adjoining reefs, at a less depth, contained many of them. They do not, therefore, rise from the deep bottom to near the surface. Finally, the islands of the Red Sea are everywhere evidently diminishing, instead of increasing, at their surface.

Ehrenberg concludes his interesting treatise with the remark, that the corals in this sea do not indeed appear to be the constructors of new islands, but rather as maintainers of those already existing.

Let us now turn to the numberless coral islands in the Indian and Australian Oceans, respecting which we have since 1605

\* Ehrenberg in Poggend. Annal. Vol. 47, p. 502.

† Ibid. Vol. 54, p. 437.

‡ Ibid. Vol. 41, p. 1, et seq. and p. 243, et seq.

received information, sometimes bordering upon the miraculous, through a great number of navigators, and which Darwin\* has more recently made the subject of an extended investigation.

We shall direct our attention principally to the coral-banks which lie close to the coasts of continents and larger islands surrounding them, as well as the coral-reefs which surround continents or islands at a greater or less distance from the coast.

No coral-banks are found where the coasts are steep and descend deep into the sea, because there the necessary foundation for the growth of the zoophytes is wanting. Where the coasts enter the sea at a very slight inclination, the banks lose the character of an enclosure, and appear as detached, irregularly distributed patches, frequently of considerable area.

The immediate structure of the coral animals does not rise above the surface of the sea, as these animals cannot live out of the water. But, by the action of the breakers, fragments of greater or less size, even to 6 feet long and 3 or 4 feet thick, are detached from the coral mass, and thrown upon the reef. In addition to this, broken shells, fish-bones, cases of marine animals, and earthy substances, are thrown up by the waves into the interstices of the coral, and aggregate to a breccia. But the height of such reefs or islands is always small; they seldom rise more than 6 or 12 feet above the water at high tide.

According to Darwin, the corals flourish best in open seas which are in constant motion, probably from the simple reason, that these convey to them the most food (principally carbonate of lime), which, like all animals fixed to the place of their growth, they are incapable of obtaining from a distance. If they or certain kinds of them were not able to resist the force of the waves and breakers by their vitality, it would be difficult to imagine what would give stability and firmness to the entire structure. The whole foundation of an atoll on its exterior is not built up of a dead mass, but of the strong skeletons of animals which lived during its formation, although they may now be partially dead. The assumption of Forster and other naturalists, that the coral animals built up their structure from unfathomable depths, is destitute of every kind of probability. The coral animals which build reefs are not able to live at a depth of more than 200 feet. At the same time, they have been found at much greater depths, as well as on the exterior of atolls and on submarine reefs, entirely dead.

\* The Structure and Distribution of Coral Reefs, &c. London, 1842.



C. Stokes\* remarks that corals brought up by the dredge from 270 fathoms, lat.  $72^{\circ} 31' S.$ , long.  $173^{\circ} 39' E.$ , consisted of three species, of *Lepralia*; *Retipora cellulosa*, a small piece in a perfectly fresh and living state; a *Reptora* or *Hornera* in similar fresh condition. Fragments obtained by soundings from 400 fathoms, lat.  $33^{\circ} 31' S.$ , long.  $107^{\circ} 40' E.$ , consisting of pieces of shell and small corals, appear, however, not to have been brought up in a living state. Although, he says further, "we have long known that a *Primnoa*, from Norway, is found at a great depth and some other corals have been taken at from 70 to 100 fathoms; yet it is rare, as far as our present knowledge instructs us, to find any corals, except, perhaps, some of the Celleporæ, at great depths; and I am not aware of any previous instance of a *Melitoca* or a *Madrepora*, at all resembling those here represented, having been found except at small depths, and in a warm climate; from which I had concluded that they required more of the solar light and warmth than they could obtain at the depth from which you took those specimens. *Primnoa lepadifera* is found, I believe, only on the coast of Norway. I have specimens nearly two feet in height, which were presented to me by Sir Arthur de Capell Brooke, who collected them there. He received accounts of their growing to a much larger size. They are found at great depths, varying from 150 to 300 fathoms. At these depths they grow in company with a large branching *Alcyonium* of a red colour."

Darwin came to the conclusion that a very extensive region of the Australian world was and still is gradually sinking.† From this it would be easy to conceive that limestone rocks, thousands of feet in thickness, like our Jura, might be the work of the coral animals, if the sinking of a reef continued during long spaces of time, and the animals meanwhile continued to build. The extent of our limestone formations cannot be any obstacle to this mode of explanation; for the Jura, for example, has only  $\frac{3}{4}$  the length of the coral-reef which surrounds New Holland. The circumstance that the coral islands have not suffered any alteration during 250 years, can have no weight, for what is  $2\frac{1}{2}$  centuries compared to the great geological periods? And the deposition of a limestone stratum, like that of the Jura, which took from sea-

\* Remarks on some corals obtained from great depths in the Antarctic Ocean, in a letter from Charles Stokes, Esq. to Captain Sir James Ross, R.N. Jameson's Edinb. New Philos. Journ., July to October, 1847, p. 258.

† For objections to this view, see Lyell's Principles of Geology, seventh edition, p. 760.

water containing about only  $\frac{1}{10000}$  carbonate of lime, certainly requires a long period.

Various phenomena which our limestone formations present, their frequent interruption, and the circumstance that the causes which, for example, produced the *grauwacke* limestone could not have been in action during the formation of the *grauwacke* itself, &c., would be explained by the circumstances of the occurrence of the coral-banks and reefs.

The fact that the coral animals build only in the clearest and purest sea-water, is important in reference to the stratification of limestone upon sediments of mechanical formation. The frequent occurrence of pure sedimentary limestone containing only traces of foreign admixtures, favours the opinion that they must have been formed from pure sea-water. The presence of suspended particles of carbonate of lime in sea-water cannot be conceived, even if it may be sometimes conveyed in such a strata to the sea by rivers, as it is far from its point of saturation, and contains free carbonic acid.

However much these relations may coincide with the view that a limestone formation, like the *Jura*, may have been produced by coral animals, still they can scarcely have been such coral animals as those which now build reefs; for these require a tropical climate. Whether the above-mentioned corals found in the North Sea, and at a great depth, build reefs, is not known; it is, however, sufficient to be able to consider this as a possibility.

Finally, it must not be overlooked, that sediments formed by organic agency may occur, mixed with mechanical sediments. I have analyzed two tile slates from one of the uppermost sections of the Devonian system in Westphalia, and found them to contain 25 to 26% of carbonate of lime. It can scarcely be doubted that the clay-slate mass was deposited from the sea simultaneously with the carbonate of lime. Thus, the carbonate of lime was separated by organic agency, while the sea was turbid from the suspended clay-slate particles. This separation cannot, therefore, have been effected by coral animals which build only in clear water.

In the open sea none of the conditions are present under which separation of carbonate of lime from water takes place; it separates from the water of the Carlsbad springs, containing about 3 times as much as sea-water, because the water is unable at its high temperature, ( $167^{\circ}$  F.), and ordinary atmospheric pressure, to retain the carbonic acid which held it in solution; it separates

from cold water as a calcareous sinter when the water is stagnant, carbonic acid and the water itself evaporating. If, however, the water flows rapidly into brooks and rivers, where it is further diluted, no deposition may take place.

Simple observations, which ordinary spring-waters admit of, show what conditions must be present in the sea in order that carbonate of lime may be separated from it. The spring in the chemical laboratory at Bonn receives its water from the Rhine, and contains 0.0275% carbonate of lime, consequently about  $2\frac{3}{4}$  times as much as sea-water. In order to ascertain at what point of concentration the separation of carbonate of lime would take place in the water, when evaporating at an ordinary temperature, 10,000 grains were exposed in a room, not warmed, from February to April. After two months the water had commenced to becloudy, and after three months the cloudiness had so far increased that a quantitative determination of the precipitate could be made. During this time, 3,237 grains of water had evaporated; the residue, therefore, amounted to 6,763 grains. Upon the glass a rim of crystalline carbonate of lime had been deposited; the entire quantity of this, and what was suspended, amounted to 1.06 grains, and the quantity remaining in solution was 1.05 grains. With this carbonate of lime, 0.18 grains of silica had also been separated. Both the precipitates gave a solution with hydrochloric acid, which was slightly turbid from the presence of silica.

When, therefore, sea-water deposits carbonate of lime, about 0.75 must have previously evaporated; but when about 0.375 parts have evaporated, the separation of the sulphate of lime commences. If, therefore, the sedimentary limestones have been produced by the evaporation of sea-water, they should contain more sulphate than carbonate of lime, which is by no means the case.

It is self-evident that an evaporation, which would reduce the mass of a sea to  $\frac{1}{4}$ , could only take place in detached lakes. It may also be conceived as possible in a sea connected with the ocean by a strait, if, as in the case of the Mediterranean, a constant influx from the ocean takes place, and the evaporation was greater than the influx.

On evaporating sea-water from the German Ocean at a boiling-heat, I found that it did not begin to become turbid until 17.13% had evaporated. Even this separation of carbonate of lime could not take place by evaporation at ordinary temperatures, even supposing that the influx of rivers and meteoric water were to cease until such a quantity of water had evaporated; for it is not the

concentration of the water, but the dissipation of the carbonic acid after continued boiling, by which this separation is effected. As I found in 10,000 parts of this water 0·57 parts carbonate of lime, which is about 1-18th of the quantity contained in a saturated solution, the separation would not commence until 17-18ths of the water had evaporated, inasmuch as in the evaporation at ordinary temperatures none of the carbonic acid, which held the carbonate of lime in solution, escaped. But this water contains five times as much carbonic acid as is necessary for the solution of the carbonates of lime and magnesia.

These inferences were confirmed by experiment. On leaving this water to evaporation at ordinary temperatures, crystals of sulphate of lime made their appearance first after 0·75 of the water had evaporated. The thin crust of salt which had separated upon the sides of the vessel, did not effervesce in the least with acid. By further evaporation, more sulphate of lime was separated, and subsequently cubes of chloride of sodium; but still there was no appearance of cloudiness from the separation of carbonate of lime, and it was not until the dry residue was redissolved in a small quantity of water, that the liquid was slightly turbid from the suspended carbonate of lime and silica.

But is it necessary that such considerable quantities of water should evaporate in order that carbonate of lime should be separated? May not this take place in consequence of the escape of carbonic acid with the evaporating water? However, in this case the separated carbonate of lime would be immediately redissolved by the free carbonic acid of the inferior strata of water.

The assumption that sea-water contained a larger quantity of carbonate of lime at the period of the formation of the great limestone strata from the transition limestone to the chalk, and that the increase of limestone formations during this period was a consequence of the decrease of this carbonate in sea-water, is contradicted by the circumstance that it would then have been impossible that a solution should have been left which is so far from saturation as the sea-water of the present time; for all precipitations which result from the evaporation of solutions leave a saturated mother-liquor.

It is therefore evident that in every point of view the assumption that our great limestone strata, from the grauwacke limestone to the chalk, have resulted from the evaporation of sea-water, is altogether unfounded.

At the period of the sedimentary formations, as at the present time, the rivers uninterruptedly carried carbonate of lime into the



sea. Not only the older limestone strata, which had already been elevated from the sea, yielded carbonate of lime, but also the crystalline rocks by the gradual decomposition of their calcareous silicates by the carbonic acid of the atmosphere. There is probably no river-water which contains less carbonate of lime than sea-water; many river waters contain four times as much.

At the mouth of several rivers, sand and detritus in the sea are cemented by the carbonate of lime to hard rocks, and considerable beds of limestone are deposited. Where in the deltas of rivers pools are formed when the water is low, whose water evaporates entirely in warm seasons, the conditions for the depositions of carbonate of lime are particularly favourable; these pools are again filled when the water increases, and again dried up during the hot weather, and by this frequently-repeated alternation the calcareous deposits continually increase. Lyell\* directs attention to the fact that the fresh water introduced by rivers, being lighter than the water of the sea, floats over the latter, and remains upon the surface for a considerable distance; consequently, it is exposed to much evaporation, and carbonate of lime is deposited.† That a great proportion, at least, of the new deposit in the delta of the Rhone consists of rock, and not of loose incoherent matter, is perfectly ascertained. In the museum at Montpellier is a cannon taken up from the sea near the mouth of the river, imbedded in a crystalline calcareous rock.

Even on those coasts where there are no rivers falling into the sea, but where the waves are driven by strong winds far into the land, leaving in their backward passage sea-water enclosed in hollows, the evaporation gives rise to the formation of calcareous deposits, which are increased by the frequent alternation of influx and evaporation of the sea-water. Such deposits will occur everywhere on coasts in hot zones, where more water is removed by evaporation than is conveyed thither by currents and wind. Von Buch's‡ description of the still-continued formation of conglomerates on the sea-shore, between the town Las Palmas, on the Canary Island, Gran Canaria, and the small island Isleta, is of especial interest.

\* Principles of Geology. Seventh edition, p. 259.

† It is, however, to be observed that even the greatest quantity of carbonate of lime in Rhone-water (p. 76), is only 1-7th of that contained in water saturated with this carbonate. A very considerable quantity of Rhone-water must, therefore, evaporate before carbonate of lime can separate.

‡ Physik. Beschreibung der canarischen Inseln. 1825, p. 258; also pp. 260 and 302.

In order to form a conception of what testacea are capable of effecting by organic agency, I determined the weight of ten oysters and their shells. After they had been opened, the enclosed sea-water was as far as possible removed. The weight of the shells varied from 2·78 to 7·57 that of the oysters. The weight of the oysters, however, must be too high, as they were not dried. No one can doubt that it was the carbonate of lime dissolved in the sea-water which alone furnished the material for the formation of these shells. If, now, we assume that the sea-water contains about  $\frac{1}{10000}$  of carbonate of lime, and that the oysters are capable of deriving all their calcareous substance from the water by organic agency, it follows that the above number of oysters required for the formation of their shells from 345 to 587 pounds, or 5·2 to 8·9 cubic feet of sea-water. This quantity is from 27,760 to 75,714 times the weight of the shells.\*

According to these results, an oyster would appear to be, as it were, a pumping-machine of extraordinary activity and production. It is also known, that in testacea there is a continual current of water, from behind forwards, within the mantle. If, as is probable, only a part of the carbonate of lime in these animals be separated from sea-water by organic agency, the quantity of water which is taken up by them would be still greater. This current of water in the oysters appears to be astonishing, when we compare it with the quantity of fluid which passes through the human body. When a man, weighing 150lbs., consumes even 5lbs. of liquid daily during a period of 75 years, still a quantity of liquid only 912·5 times the weight of his body would pass through his organism; or, only 1-30th to 1-83d of the sea-water which has passed through the oysters. Although oysters have a tolerably long life, still their shells are probably formed in a few years, perhaps in still shorter time. If, moreover, only a minute quantity of the carbonate of lime in the sea-water which passes through them, is consumed in the formation of the shell, it is very possible that a current of water passes through oysters which is several hundred, or even

\* We have already mentioned (p. 80) that the quantity of carbonate of lime annually conveyed to the sea by the Rhine, would yield the material for 332,539,000,000 such oysters. Immense numbers of crustacea may, therefore, be produced annually in the sea without the quantity of carbonate of lime in the water being diminished. Forchhammer communicated to me his opinion that the testaceæ also decompose the sulphate of lime in sea-water, by carbonate of ammonia formed by their organic agency. But sulphate of lime might, perhaps, likewise be decomposed by the organic matter of marine animals into sulphuret of calcium, which would be decomposed by the carbonic acid produced by them.

thousand times, greater than the liquid which a man consumes in the same time.\*

The quantity of carbonate of lime which the oysters alone separate annually from the sea, is not inconsiderable; there are oyster-banks of great extent. If the corals and other animals which separate lime possess only such an organic power as the oysters, we can understand what quantities of carbonate of lime can be abstracted annually from the sea by these animals, and what structures may be built up by the former.

From the free carbonic acid in sea-water, it might be conjectured that the shells of marine animals are redissolved after their death; but their occurrence in sedimentary formations, the formation of limestone in the sea, and especially that of coral-banks, show that the calcareous structures formed by organic agency resist this solution in a high degree. What is it, then, that renders this solution so difficult? On exposing fresh oyster-shells to the action of carbonic acid under water for 24 hours, it was found that 1,000 parts of water saturated with carbonic acid had dissolved of

Lamina from the interior of the shells ....	....	....	0·028
The same powdered ....	....	....	0·160
Chips from the exterior ....	....	....	0·070

The laminæ from the interior of the shells require, for solution, 36 times as much carbonated water as chalk, and 100 times as much as precipitated carbonate of lime; the chips from the exterior 14 times as much as chalk, and 40 times as much as artificial carbonate. The interior part of the shell is, therefore, less soluble than the exterior. The crystalline condition of carbonate of lime has no essential influence upon its solubility; for 1,000 parts of water, saturated with carbonic acid, dissolved 0·42 parts of powdered calc-spar; consequently, 15 times as much as from the lamina of oyster-shells. It is, undoubtedly, the animal matter which makes the oyster-shells so difficultly soluble.

Quenstedt† remarks, that after treating a fresh shell with diluted hydrochloric acid, a gelatinous mass remains, having the form of the shell, and that shells of the pre-historic time effervesce more strongly with acid than the living animals, which, after solution, leave no gelatinous mass. Experiments which I have made

\* Kröyer (Edinb. New Phil. Journ. 1840, No. 57, p. 24) states that the place best adapted for the development of oysters is a flat, firm bottom, at a depth of from 5 to 15 fathoms, where the current is not violent; too strong a current carries away the young brood.

† Petrefactenkunde Deutschlands. Vol. 1, Abth. 1, p. 6.

show, that the membranes between which the carbonate of lime is enclosed in oyster-shells, protects it in a high degree against the attack of dilute hydrochloric acid. But if even this acid dissolves the shell so slowly and with such difficulty, although its penetration is favoured by the carbonic acid escaping and rending the membrane, it is evident that the action of the small quantity of carbonic acid in sea-water, which is not aided by this circumstance, must be almost null. The reason that the shells are less soluble in *laminæ* than in powder, is, that in the former the calcareous substance is surrounded by the membrane, and exposes only a few points of contact; but in the perfect shells, there are scarcely any exposed points. The possibility of the formation of sedimentary limestone, is consequently dependent upon the simple and necessary relation, that marine animals separate carbonate of lime from sea-water in vessels which are insoluble in water. As in the true and important coral animals the soft parts are external, and the tree-like skeleton interior, the carbonate of lime in these animals appears also to be protected by the animal matter.

The carbonate of lime is thus subjected to a wonderful circulation. The marine animals separate it from sea-water, and protect it against the dissolving influence of the latter. In this way calcareous sediments are formed, which are elevated above the surface of the sea. Then the organic matter is gradually destroyed, the carbonate of lime is again exposed to the solvent action of the meteoric waters containing carbonic acid, and is thus removed and carried into the sea, again to renew the same cycle of changes.

If there were in the sea no animals which build calcareous structures, the carbonate of lime conveyed to it by the rivers would, after a little, accumulate to such an extent that a chemical separation must finally take place. Such a circumstance may possibly have taken place in the earlier periods of our earth, previous to the existence of animals. If at that time the rivers conveyed carbonate of lime to the sea, as at present, or if at the time when there were neither dry land nor rivers, the sea-water decomposed rocks containing calcareous silicates at the bottom of the sea and dissolved carbonates of lime, a state of saturation must finally have been attained, and beyond this a chemical separation of the carbonate of lime. If at that time there could not have been any limestone rocks, there was still no want of materials, for it is to the rocks containing calcareous silicates that we must trace the origin of all the carbonate of lime upon the earth.



According to the present condition of science, this is the only conceivable way in which it is possible to account for the formation of sedimentary limestone without organic agency. The so-called primitive limestone in slate, destitute of organic remains, may have been formed thus. The graphite and dark-grey colour of this limestone, which is in all cases owing to organic remains, must then be ascribed to a vegetation which had existed and disappeared previously to the appearance of animals. The testacea appearing in the sea subsequently to the chemical formation of sedimentary limestone, would have found a sea-water saturated with carbonate of lime, for the formation of shells. This rich supply would have given rise to the formation of the first limestone, whose origin is ascribed to the remains of conchifera and zoophytes, namely, the considerable and widely-distributed grauwacke limestone-beds. By this means the quantity of carbonate of lime in sea-water would have been gradually diminished, until it finally reached the present amount.

It would appear as if magnesia, which so closely resembles lime, were entirely unsuited for forming the skeletons of infusoria. At least, this earth had not formerly been found in the shells of infusoria.\* But more recently, Forchhammer has detected carbonate of magnesia in limestones of organic origin (Chap. XXIV). However, these quantities cannot be an equivalent of the carbonate of magnesia conveyed into the sea, when they are compared with that contained in sea-water and those immense quantities of carbonate of lime which are separated by organic agency.

The occurrence of magnesia in formations produced by organic agency only in such small quantities, and its entire absence in the greater number of cases, is in perfect correspondence with the fact, that this earth exists only in small quantities in the solid and fluid parts of animals, and in much smaller proportion than lime. On the contrary, in the rucoid marine plants, which, according to Forchhammer, contain in the dry state, on the average, more than  $1\frac{1}{2}$  of magnesia, the quantity of this earth exceeds that of the lime.† Thus considerable quantities of magnesia would be deposited in the strata which receive the inorganic remains of these plants. Thus the vegetable and animal kingdoms separate these two earths from one another. But both concur together in

\* German Edition. Vol. 1, p. 982.

† Silicate of magnesia appears to behave like carbonate of magnesia; for it occurs as the petrifying material of vegetable remains. However, I am not aware that silicate of magnesia occurs as a petrifying material of animal remains.

again directing the excess of these earths to the formation of mineral substances.

The organic agency which brings about in such an admirable manner the deposition in corals and marine-shells of the relatively minute quantities of carbonate of lime in sea-water, which cannot be separated by any known chemical processes, likewise effects the abstraction of silicic acid from sea-water. The important discoveries of Ehrenberg\* have not only proved the existence and uninterrupted activity of imperceptibly small microscopic organisms, even in the immediate neighbourhood of both poles, where higher forms no longer exist, but the microscopic organisms of the Antarctic Sea collected by Sir James Ross contain an abundance of entirely unknown structures. Even in the fragments of floating ice, in a latitude of  $78^{\circ} 10'$ , there were found more than fifty species of siliceous *polygastria*, and even *coscinodiska*, with their green ovaries, therefore certainly living and successfully withstanding the extremest cold. In the Gulph of Erebus there were 68 siliceous *pologastria* and *phytolitharia*, and with them only one calcareous *polythalamia*, brought up by the sounding-lead from a depth of from 1242 to 1620 feet.

By far the greater number of the microscopic marine forms hitherto observed are siliceous. But it is not in merely individual spots and in inland seas, or in the neighbourhood of coasts, that the ocean is densely peopled with these organisms; according to Schayer, it was found to be so with the water examined by him on his return from Van Dieman's Land, in  $57^{\circ}$  lat., south of the Cape of Good Hope, as well as in the Atlantic sea between the tropics. It may be considered as proved, that the ocean in its ordinary condition, without special colour, without the fragmentary floating filaments of the siliceous fibres of the genus *Chartoceros*, and resembling the *oscillatoria* of our fresh water, and in its most perfect transparency, contains numerous individual microscopic organisms. Some *polygastria*, found on Cockburn Island mixed with penguin excrement and sand, appear to be distributed over the entire earth, others are common to both poles.

Even if silica had not been found in a state of solution in sea-water, there could not have been any doubt that it was from dissolved, and not suspended silica, that these organisms constructed their shells. According to Ehrenberg's investigations and calculations, there are formed annually in the mud deposited

\* Ueber das kleinste Leben im Ocean, eine in der Acad. der Wissenschaften zu Berlin, am 9 März, 1844, gehaltene Vorlesung.

in the harbour of Wismar, in the Baltic, 17,496 cubic feet of siliceous organisms. Very considerable quantities are likewise formed in the harbour of Pillau. If such developments of infusoria at the cost of the silica in sea-water still take place, there can be no grounds for assuming the existence of larger quantities of this substance in the seas and fresh-water lakes of previous epochs. When we call to mind that these siliceous formations constitute beds of earth many fathoms in thickness and miles in extent, their geological importance is self-evident.\* We see that, by the action of vital agency, those substances which exist in the smallest quantities in sea-water are separated, and that nature employs this means in order to produce sedimentary formation where inorganic processes are very nearly or entirely incapable of acting. The phosphate of lime, and the fluoride of calcium are separated with carbonate of lime by the coral animals; from the dissolved silica the infusoria form their sheaths; coral-banks of immeasurable extent, and thick siliceous strata, are the final results of these organic processes.

Among the youngest formations is the mountain meal; among the tertiary are the polishing slate, and the semiopals of the polishing slate, which consist partially or entirely of the sheaths of the mailed infusoria.† Among secondary formations there are many chalk strata, perhaps all the European, which consist of microscopic, snail-like coral animalcules with calcareous shells, for the most part entirely invisible to the naked eye, and of others with siliceous shells from 1-24th to 1-288th of a line in magnitude.

The traces of similar phenomena have, as already mentioned (p. 173), been detected even in the older sedimentary limestones.

Many chalk marls, as for example, those in the Teutoburger Wald,‡ contain, besides 26% carbonate of lime, 59% silica. The rock which contains them is traversed by numerous fine rectilinear pores in all directions. They are finer than a hair, as much as 3 lines in length, and are probably the spaces in which the needles of *Amorphozoa* have existed.§ It would appear that in this case there

\* The siliceous infusoria form a mouldy covering, about half an inch thick, upon stagnant water during warm weather. Although more than 100,000,000 of these animalcules weigh only 1 grain, still Ehrenberg collected in an hour nearly 1 pound of them. Poggend. Annal. Vol. 41, p. 557.

† Ehrenberg, Poggend. Annal. Vol. 38, p. 463.

‡ A. Römer, Norddeutsches Kreidegebirge, p. 122.

§ The *Amorphozoa* appear to belong rather to the vegetable than the animal kingdom. Rejected by zoologists as well as botanists, they remain intermediate between the two kingdoms. Bronn, Handbuch einer Geschichte der Natur. Vol. 3, Abth. 2, p. 78.

has been a simultaneous separation of carbonate of lime and silica by organic agency, if indeed there has not been a displacement of the former by the latter.

Ehrenberg declared that the layer situated under Berlin, consisting for the most part of siliceous infusoria, and frequently containing living animalcules, was the thickest among known fresh-water formations, since it exceeds by three times the bed in the Lüneburger Haide, 28 feet thick, and hitherto the thickest known.\*

Ehrenberg calculates that of the hitherto known *Polythalamia*, or so-called *Nautilæ*, in the chalk, there are frequently upwards of a million in each cubic inch, consequently upwards of 10 million in a pound of chalk. According to this, the weight of one of those animalcules is at the utmost 0·000576 grains. If we take this weight to be equal to that of their siliceous sheaths, then, if the quantity of silica in sea-water amounts to  $\frac{1}{33333}$ , this formation of 0·000576 grains of silica would require 19·2 grains of sea-water, supposing that the whole of its silica were abstracted. This quantity of sea-water, about 19 drops, occupies a considerable space, when we compare it with the range of action of infusoria 1-24th to 1-28th of a line in diameter, and which at the moment of their development are much smaller. Such an animalcule must therefore consume 33,333 times as much water as it weighs, in as far as it assimilates all the silica in the sea-water. But if, as is probable, only a small part of this silica is fixed while passing through the organisms of these animalcules, this multiple will be increased perhaps very considerably. If, finally, the rapid development of such infusoria be remembered; if we assume 24 hours as its duration, then during this time at least, the 33,333-fold weight of water passes through their organisms. This is as much as if a man 150lbs. in weight passed through his body in 24 hours, 5 million pounds of water, *i. e.* near a cubic foot in a second—a quantity with which an overshot mill-wheel might be driven.

The infusoria are, therefore, to be compared to a pumping apparatus which uninterruptedly absorb water, from which by means of a very energetic secretory power, they assimilate the substance dissolved in it, which they require as food, or for the formation of their shells.

According to Ehrenberg's investigations,† there are placed round the mouths of these animalcules, hairs, which form a crown

\* Poggend. Annal. Vol. 54, p. 437.

† Naturgeschichte der Infusionsthierchen nach Ehrenberg's grossem Werk, über diese Thiere, &c. Von Gravenhorst. 1844.



of cilia or rotatory organ, by the motion of which a whirl is produced in the water, towards the mouth, the immediate purpose of which appears to be the obtaining of food, but also to serve as a means of progression. The whip-formed proboscis of many *polygastriæ* has the same purpose, for by the motion of it a whirl is likewise caused in the water. In those animalcules which have been found to possess internal organs of nutrition and digestion, these appear as several bladder-like stomachs which present a large surface for the absorption of water, and the separation of its constituents.

These phenomena show how incomparably greater were the effects which nature produced by microscopic organisms, than were those which were attained through the larger animals. Here is a minimum form of existence acting as a cause, and maximum effects resulting. The greatest results produced with the smallest expenditure of means. In no case can the distance between the insignificance of the means and the immensity of the effects be greater than in that of the infusoria forming limestone and siliceous strata.

The deposition of silica in the infusoria, whether we consider it as a purely chemical action, perhaps caused by the known tendency of this acid to combine with organic matter, or as a contact action of the organs of these animalcules, it still exceeds our comprehension, how, in so small a range of action as that of the individual infusoria, such comparatively great quantities of material can be brought into play in so short a time. But in creatures which multiply with such extraordinary rapidity as the infusoria, all the functions must proceed with uncommon rapidity. According to Ehrenberg's observations of *Hydotina senta* during 18 days, such an individual is capable, under favourable circumstances, of a fourfold multiplication during 24 to 30 hours. It can, during this time, develop four eggs; but this four-fold increase during one day goes, when no obstacle intervenes—and the one animalcule lays 40 eggs in 10 days—into the 10th power; thus, on the 10th day there would be a million of individuals from one mother, on the 20th day a billion, on the 30th day a trillion, &c. Although this fecundity of the *Rotifera* is the greatest which has been observed in nature, it falls far short of that of the *polygastria* infusoria. Ehrenberg observed a *Paramœcium Aurelia* which was  $\frac{1}{12}$  line large during its life of several days, and recognized the eight-fold increase of an individual during 24 hours, by simple tranverse partition; which would indicate the possibility of

double that increase. But as these animals increase by eggs as well as by partition, and these eggs are deposited not singly but in masses, it follows that the possible increase of a single individual during 48 hours is so enormous that it is not to be expressed in numbers.\*

Nature as it were guarding against the extinction of infusoria, which are consumed by millions as the food of larger animals, and are exposed to so many casualties, bestowed upon them this marvellous fecundity. In fact, this is greater than the material for production.

If, as previously, we take the weight of the siliceous or calcareous sheaths of an infusorial animalcule from the chalk, as 0.0005 grain, and trace the increase of those *Rotiferæ* up to the 30th day, or the 30th power, we obtain a trillion of individuals from one mother. The weight of the sheaths of these amounts to 65,000 pounds, and if they have the density of mountain-meal, about that of water, we obtain, on dividing this number by the weight of a cubic foot of water, nearly 1000 million cubic feet. A single one of these animalcules can, therefore, increase to such an extent during one month, that its entire descendants can form a bed of silica 25 square miles in extent, and about  $1\frac{3}{4}$  foot thick.

As a parallel to Archimedes, who declared that he would move the earth if he had a lever long enough, we may say, give us a mailed animalcule, and with it we will, in a short time, separate all the carbonate of lime and silica from the ocean.

The remarks which we have previously made (p. 177), upon the separation of carbonate of lime from sea-water by evaporation, applies in general also to silica, in as far as that conveyed to the sea by rivers may separate in this way. It must not be forgotten, that after the evaporation of a third part of the well-water (p. 177), a small quantity of silica really did separate. But here also we encounter the above-mentioned difficulties. As there are facts to prove that its separation is effected by organic agency, it may be considered probable that it is in this way alone that the balance is restored.

It is a wise provision in the economy of nature, that where purely chemical processes are incapable of effecting the separation, organized beings undertake the task. In this way infinite results are obtained with the least expenditure of means. In the first infusorial animalcule was placed the mysterious power of separating the carbonate of lime and silicic acid from the sea without

\* Poggend. Annal. Vol. 24, p. 21.

precipitants or interchange of constituents. This power descended to all its progeny, and will continue to be transmitted so long as they exist.

We have already alluded to the possibility, that it is especially the remarkable affinity of organic matter for silica which renders possible the separation of the latter from the sea-water taken up by the infusoria. But we must always consider this affinity as subject to the yet unfathomed conditions which we call vital agency; for there are silica and organic matter likewise present in sea-water, as well as in the organs of these animalcules, without this reaction taking place.

I have already alluded to the separation of carbonate of lime from sea-water by marine plants.\* This phenomenon has since been minutely examined by chemical researches.

R. Ludwig and G. Theobald examined the deposits of the brine-spring at Nauheim,† taken from an open canal, 696 metres in length, at different distances from the spring. Along this canal the brine passes very slowly, and on its way cools down from 89° to 68° F. The following are the analyses:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Carbonate of Lime ... ..	35.40	65.41	83.55	87.81	92.69	90.13	93.64	87.33	86.54	83.42
„ of Magnesia ... ..	...	1.20	2.49	9.05	4.08	5.22	5.29	10.80	10.49	11.69
Peroxide of Iron ... ..	44.28	} 8.93	2.07	} 2.05	2.15	3.17	0.75	0.62	1.62	1.96
Peroxide of Manganese ...	2.11		5.49							
Sulphate of Lime ... ..	...	...	...	...	...	...	...	...	...	0.21
Silicic acid ... ..	2.65	trace	3.09	trace	trace	trace	trace	trace	trace	trace
Arsenic acid ... ..	1.05	trace	ferruginous	...	...	...	...	...	...	...
Remains of plants & Diatomæ	...	...	...	0.12	0.01	trace	...	1.15	0.20	1.12
Water ... ..	14.32	3.90	} 3.28	0.97	1.07	1.23	} 0.32	0.10	1.15	1.60
Loss ... ..	0.19	0.56				0.25				
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

I. Deposit, at the commencement of the canal. It is separated into delicate plates, parallel to one another, and which possess a somewhat firmer consistence than the ochrey parts which lie between them. The plates are covered by a light yellow membranous felt, which consists of *microhalva firma* Breb., and in which are found in pretty considerable numbers moving siliceous *diato-*

\* Bischof, German Edition, Vol. 1, p. 953.

† Poggendorff's Annal. Vol. 87, p. 91.

*maceæ*. Farther down the canal, the development of the algæ increases considerably; they cover the bottom and walls of the canal with felt-like pellicles, and from them, in the sun's rays, is developed oxygen gas in numerous bubbles. These pellicles give rise to a botryoidal structure in the sinter which is deposited, and form upon the bottom of the canal a carbonaceous mass, which in the air emits an extremely unpleasant odour. In this mass there is a minute quantity of protoxide of iron, which has no doubt arisen by deoxidation, by means of the carbon.

II. Small scales of firm, light-yellow and brown calcareous sinter, in which the plates present alterations according to their age and depth. Upon these scales are found microscopic rhombohedrons of calc-spar.

III. Calcareous sinter, which is deposited 280 metres from the commencement of the canal; it forms, in the fresh state, soft, lamellar, dark-brown masses, and the felt-laminæ are very tough. The older sinter contains interlying white lamellæ, in which the decaying *confervæ* seem, as in the above instance, to have reduced the peroxide to protoxide of iron, which has been removed as carbonate by the carbonic acid in the water.

IV. Light-yellow fibrous sinter, in thick shales or plates, which consist of countless microscopic crystals. From this place (400 metres) onwards grow beautifully green velvet-like *confervæ*, which appear ranged upon one another in the form of threads; the lower extremities of these threads pass into the calcareous sinter; the other, or green extremities, project upwards.

V. More compact calcareous sinter, like marble, deposited 620 metres from the commencement of the canal.

VI. Sinter deposited at the distance of 696 metres; it is shaley, reniform, fibrous, transparent, and marble-like; lighter-coloured lamellæ alternate with brown layers; the surface is covered with rhombohedrons, and contains *confervæ*.

VII. Tubes of sinter, formed in tin tubes, which stood in the canal; they are light-yellow, transparent, marble-like, and have their interior sowed over with rhombohedrons. In the lower parts of the brine-canal the black carbonaceous mud does not occur in so great a quantity as in the parts nearer the spring.

VIII. Sinter, consisting of small rhombohedrons, which incrust the algæ growing in the reservoir into which the brine flows. Upon stakes which are washed by the water, coralloid forms grow all round to the length of  $\frac{1}{2}$  or  $\frac{3}{4}$  metres. The bottom of the reser-



voir is covered with a carbonaceous mud, upon which lies a whiter and looser mud; the latter consists of myriads of small rhombohedrons.

IX. Calcareous sinter, from a subterranean canal, which in like manner is covered with confervæ.

X. Sinter from this canal, where it opens into a brook and forms a small cascade; it is brittle, and consists of an aggregate of rhombohedrons whose foliaceous structure resembles that of many dolomites. When dissolved in acids, there are left behind compact thick felts composed of plants.

The analyses of these deposits afford additional confirmation of what was above said (p. 150) in regard to the sequence of such deposits from warm springs; they lead, however, to still more important conclusions.

From the analysis communicated in Chapter XVIII, of the Soalsprudel at Nauheim, it follows that the magnesium is combined with chlorine merely.\* The not inconsiderable proportion of carbonate of magnesia in the calcareous sinters which are associated with the growth of confervæ in the brine, is therefore very remarkable.† It may be conjectured, with much probability, that these confervæ decompose the chloride of magnesium contained in the water, and convert it into carbonate of magnesia. The brine which flows out of the reservoir is also actually found to contain only 0.0095% chloride of magnesium, therefore 0.0244% less than the brine-spring. Since only about 0.65 of the decomposed chloride of magnesia of the brine is again found in the sinters, a portion of this chloride would, therefore, appear to be taken up by the plants. In the brine-canal, while the proportion of chloride of magnesium diminishes, that of the chloride of calcium increases; for in the brine-spring the latter amounts to 0.1935%; in the brine in the reservoir, on the other hand, to 0.2527%. It appears, therefore, that plants can effect an interchange between the constituents of the chloride of magnesium and carbonate of lime, whereby carbonate of magnesia and chloride of magnesium are formed.

\* When the clear water of the Soalsprudel was slowly evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent the chloride of magnesium from being decomposed, and the dry mass was treated with water, to dissolve the soluble constituents, the residue contained scarcely any traces of carbonate of magnesia.

† In the deposits formed from the brine upon the thorns of the graduation-houses, I found likewise, along with 98.82 per cent. carbonate of lime, 0.12 carbonate of magnesia. But here also grows *Glocotila oscillaria*, although only sparingly.

Since plants decompose in the sun's rays the atmospheric carbonic acid into oxygen which is disengaged, and into carbon which serves for their nourishment, such plants as grow entirely submerged in water extract the carbonic acid from the water only. One of the two equivalents of carbonic acid in bicarbonate of lime is combined by only a feeble affinity, for it is disengaged even during the evaporation of water in which that salt is held in solution. Since now the neutral carbonate of lime is precipitated upon the plants growing in the brine in question, and, according to the researches of Ludwig and Theobald, the evaporation of the water takes no share in the formation of the sinter, no other view remains than that these plants take up an equivalent of carbonic acid, and decompose it into oxygen and carbon. The decrease in the amount of vegetation towards the lower parts of the course of the brine speaks in favour of this view, inasmuch as the proportion of carbonic acid also diminishes in these parts. The oxygen set free during the decomposition of the carbonic acid oxidises the protoxides of iron and manganese, the carbonic acid with which they were combined being liberated, and in this way a farther quantity of carbonic acid is furnished.

The silicic acid in the brine-spring at Nauheim appears to be separated by the countless siliceous *diatomaceæ* living in it. In regard to these, it is not known with certainty whether they belong to the animal or to the vegetable kingdom.

Evolutions of oxygen gas, from organic deposits from brines, were already observed by Pfankuch\* in the brine at Rodenburg, in Hesse, and confirmed by Wöhler.

On the bottom of the canals out of which the brine flows on to the thorns of the graduation-houses, there is formed, in the summer months, during continued clear and warm weather, a slimy, transparent mass; it has a tough, skin-like character, and is filled with air-bubbles, often several inches in diameter, which are so rich in oxygen that when they are collected in a bottle a piece of incandescent wood, passed into it, inflames. The numbers of these air-bubbles was so considerable as to be capable of filling many hundred bottles. According to Ehrenberg's† investigations, the membranous mass consists chiefly of living infusoria (*frustula salina*, found by him in the Königsborner brine also), which are matted together by a small alga (*hygrocrocis virescens*). In a few

\* Annal. der Chemie und Pharmacie. Vol. 41, p. 162.

† Poggendorff's Annal. Vol. 57, p. 308.

places in the brine-canals the slime had a feeble greenish colour, and in it the algæ were more developed; many infusoria were also observed in it.

The very carefully-washed pure slime yielded, on being submitted to the process of dry distillation, ammoniacal products; and, on being incinerated, left a large quantity of white ash, containing much carbonate of lime, which had been precipitated from the brine, and siliceous skeletons still retaining unaltered the form of the infusoria.\*

Here, therefore, the same appearances are shown as in the brine-canal at Nauheim; and, perhaps, if further microscopic researches were made, rhombohedrons of calc-spar would likewise be observed in the slimy mass.

Ehrenberg† had already endeavoured to prove that the organic forms, *chlamidomonas pulvisculus* and *Euglena viridis*, which Priestley employed in his memorable experiments, were, in reality, animals, and not plants. Aug. and Charl. Morren,‡ who have repeated the experiments of Priestley, found that it is *chlamidomonas pulvisculus*, together with a few other green animalcules, which develop the oxygen gas. Ehrenberg§ is of opinion that the evolution of oxygen, observed by Von Pfankuch and Wöhler, also proceeds not from plants, but from animals. The researches of Ludwig and Theobald, however, have pointed out that the oxygen which is evolved by the algæ in the brine-canal of Nauheim, proceeds from the decomposed carbonic acid of the bicarbonate of lime. Wöhler also found much carbonate of lime in the slimy mass from the brine at Rodenberg. It may be conjectured, therefore, that the oxygen which is evolved from this mass has the same origin. In this case, however, if Ehrenberg's view be correct, the carbonate of lime would have been deposited, not upon the algæ, but upon the infusoria. With this, however, the circumstance that the infusoria have not calcareous, but siliceous skeletons, cannot be brought to harmonize. Do the infusoria merely decompose the free carbonic acid in the brine? In such case, this decomposition would not be attended with a deposit of carbonate of lime, and it might then be understood how the infusoria, besides

\* Previous to this examination, the apothecary Kützing (Poggendorff's Annal., Vol. 32, p. 575) found that the mails of many small infusoria, and especially of several species of frustula, consist of silica.

† Ueber die Infusions Thierchen als vollendete Organismen. 1838, pp. 65, 108, 120, and 523.

‡ Mém. de l'Acad. de Bruxelles, 1841.

§ Poggendorff's Annal. Vol. 57, p. 314.

decomposing the free carbonic acid, also give rise to a separation of the silicic acid which is dissolved in the brine. The determination of this question, however, requires in every instance a further investigation.

R. Ludwig showed, that at Ahlersbach, in Hesse, from a weak spring which contains only 0.031% of carbonate of lime, *hypnum tamariscinum* gives rise to the formation of a layer of calcareous tufa consisting of the most elegant incrustations. The evaporation of the water has no share therein; for where the latter trickles over a rock denuded of vegetation, not a trace of carbonate of lime is deposited. In the Main, and in the Fallbach at Hanau, there grow several varieties of *cladophoræ*, which are incrustated with crystalline carbonate of lime. In two other brooks in that region grow *chara vulgaris* and *zannichellia palustris*, which exhibit the same appearances in a still higher degree. These plants, therefore, still extract carbonate of lime from rivers and brooks which are certainly very poor in that salt. In several saline waters in the above region, which are richer in carbonate of lime, there are different species of *rhizodium-vaucheria* and *oscillariæ*; and at Salzhausen is found the alga *phormidium thinoderma*, which otherwise occurs on the seacoast; all of which are incrustated with a considerable number of small rhombohedrons of calc-spar.

Ludwig\* subsequently mentioned several other observations, which show that carbonate of lime is separated by the organic agency of plants.

Incrustations of living, as well as of dead plants, by means of carbonate of lime, are neither rare nor unknown in springs and brooks. The lower portions of *hypnum commutatum* are not unfrequently found in springs to be incrustated with carbonate of lime, while the upper portions of the plant still continue to grow.† A former pupil of mine, O. Weber, found that in numerous springs in the immediate neighbourhood of Ilfeld, on the Harz, the older leaves of the mosses growing in them are coated with carbonate of lime, while the fresh green sprouts grow upwards over the incrustated masses. He found also, that a brook at Jena, which flows over a thick layer of calc-sinter, deposits in like manner incrustations upon the plants growing in it, particularly upon the mosses.

From the analyses of plants, grown in a brook, by C. Schultz-Fleeth we obtain the following results:—

\* Poggendorff's Annal.\* Vol. 87, p. 143.

† A. Grisebach, über die Bildung des Torfs. 1846, p. 36.



## I. Plants which were grown beneath the surface of the water.

	Chara fetida.		Hottonia Palustris.	Nymphæa Lutea.
Ash in 100 parts of dried plants	54.58	68.40	16.69	7.96
In 100 parts of this Ash :—				
Lime .. .. .	54.73	54.84	21.29	25.24
Magnesia .. .. .	0.57	0.79	3.94	5.09
Carbonic acid .. .. .	42.60	42.86	21.29	22.23

## II. Plants which rise above the surface of the water.

	Nymphæa Lutea.	Nymphæa Alba.	Stratiotes Aloides.	Scirpus Lacustris.	Typha Angustifolia.	Arundo Phragmitis.
Ash in 100 parts of dried plants	10.15	12.99	17.19	8.07	9.58	4.69
In 100 parts of this Ash :—						
Lime.. .. .	30.00	18.89	10.73	6.98	21.94	5.88
Magnesia .. .. .	3.61	2.67	14.35	2.38	1.56	1.21
Carbonic acid .. .. .	28.26	22.16	30.37	7.93	21.01	6.57

The greatest care was taken in cleaning the plants previous to analysis; the carbonate of lime, which incrustated the plants, can only, therefore, have amounted to a very small fraction. *Chara fetida*, on being simply dried and pulverised, yielded, when treated with dilute hydrochloric acid, 27.57% of carbonic acid; and another portion, after incineration, gave, on being similarly treated, 29.31%. The whole quantity of the lime, therefore, appears in the living plants to be combined with carbonic acid, and not with organic acids; the slight difference in the quantities of carbonic acid in the two cases may arise from the impossibility of pulverising the plants so finely as to bring every particle into contact with the acid. If the whole amount of the carbonic acid in the ash of the chara be assigned to the lime, the carbonate of lime will amount to 97.6% of the ash of the chara, or to 66.7% of the dried plant. The proportion of magnesia in some of these water-plants is also considerable; in *stratiotes aloides* it amounts, indeed, to more than the lime. The water of the brook, in which the foregoing plants grew, is, compared with most rivers, rather poor in carbonates; it contains in 100,000 parts, only 5 parts of carbonate of lime, and 1 part of carbonate of magnesia.

I remember to have observed, about 20 years ago, a very rich vegetation in the springs of the Pader and Lippe, (p. 80), which contain lime. The foregoing researches induced me to request a former pupil, W. Michelis, to procure such water-plants for me. Algæ from the Lippe springs contained small pieces of limestone and grains of quartz cemented together, not by carbonate of lime, but probably by silicic acid. They likewise contained a shell of *Lymneus pereger*, and a tubular body belonging to a larva of the genus *phryganea*. After they had been very carefully freed from these bodies, and thoroughly washed with distilled water, they effervesced very distinctly with hydrochloric acid, and yielded to the acid small quantities of peroxide of iron, a somewhat considerable quantity of lime, but no magnesia. The larva also effervesced with hydrochloric acid, and lime was extracted; it retained, however, its coherency. On very careful examination by Professor Troschel, no infusoria were to be found in these algæ. From these researches, it follows that water-plants, which it is intended to examine for carbonate of lime by acids, must previously be very carefully freed from accidental substances contained in them, in order that these may not give rise to fallacies.

Dicotyledonous and a few monocotyledonous plants which grow in the Pader springs contained none of the above-mentioned substances. After being carefully washed, one species effervesced rather strongly with hydrochloric acid; and some peroxide of iron, magnesia, and comparatively large proportions of lime, were extracted. Another species exhibited no effervescence; hydrochloric acid, however, still extracted a considerable portion of lime, and traces of peroxide of iron and magnesia.

According to the foregoing researches, there can be no doubt that the water-plants, as well as the infusoria, possess the property of separating carbonate of lime from its solution. If the different species of chara grow in lakes in considerable quantity, as in the north of Germany, and if these plants perish by putrefaction, in order to make way for a new vegetation, and this alternation continues for a long geological period, very thick layers of carbonate of lime may be formed upon the bottom of the lakes, since, according to what has been above mentioned, the *chara fetida* leaves, after its destruction by putrefaction, 54 to 68 $\frac{0}{100}$  of carbonate of lime. In the older layers of limestone which have been formed in this way, the original delicate tissue of the plants may have been so far destroyed, that they can no more be recognized. Carbonaceous substances still remain, however, and impart a more or less

grey colour to the carbonate of lime; the dark-coloured limestone may, in particular, be conjectured to have had this origin. The considerable quantities of magnesia in *stratiotes aloides* leads to the conjecture, that even dolomite itself may have originated in this way.

Tertiary formations bear the most obvious traces of having been formed by the action of plants. At Bönstadt, in the Wetterau, Ludwig found an extensive litoral layer of carbonate of lime, which was almost solely composed of incrustations formed upon water-plants (apparently a species of chara). The incrustations give quite the impression of pieces of coral. A litoral limestone at Bingen, on the Rhine, appears to be, throughout, an incrustation upon a species of chara.

Observers who dwell in the neighbourhood of the ocean will find opportunity of extending these observations.\* The algæ growing in sea-water also clothe themselves with incrustations of earthy carbonates.

The above-mentioned evolution of oxygen gas (p. 191), is in itself a phenomenon of no great geological importance, since it only gives rise, under the circumstances stated, to a higher oxidation and a precipitation of the protoxides of iron and manganese. It stands, however, in very intimate connection with the decomposition of carbonic acid by water-plants and infusoria, and in this way it takes part in a great geological phenomenon, the separation of carbonate of lime from waters.

The sediments in the sea are exposed to the continuous influence of the constituents of its water, by which an opportunity is afforded for metamorphic changes. The pseudomorphic conversion of calc-spar into bitter-spar and iron-spar, which takes place in rocks through which water filters, may also go on in the sea, as both carbonate of magnesia and carbonate of iron exist in it. I found in sea-water from the Channel  $0.0005\frac{0}{0}$  proto-carbonate of iron.† The carbonate of magnesia which is separated only in inconsiderable quantities by organic agency, may consequently be deposited in the sediments by the displacement of a corresponding quantity of carbonate of lime, and thus dolomite may be formed. Silliman, Jun.,‡ found in a compact coralline limestone  $38.07\frac{0}{0}$ ,

\* We may refer to the researches made by Morren and Lewy (p. 115), in so far as they are in connexion with the object in question.

† Flocks of hydrated oxide of iron had separated in a closed flask of sea-water, which had been kept  $1\frac{1}{2}$  year. There is, therefore, no doubt that this separation takes place in the sea so far as its water comes in contact with the atmosphere, by the motion of its waves.

‡ American Journ. of Science. Vol. 6, p. 268.

of carbonate of magnesia, while fresh coral contains scarcely 1%. Dana justly observes, that this must be attributed to circumstances in which the magnesia salt in sea-water, and the carbonate of lime in the corals, react upon each other, giving rise to a magnesian limestone. Now, I am of opinion that these circumstances are to be found in the pseudomorphic conversion of calc-spar into bitter-spar. I could not refrain from making the remark, that by such a consumption of the carbonate of magnesia, we approach very near to the solution of the problem, what becomes of the not inconsiderable quantities of this substance which are constantly conveyed to the sea?

The inorganic structures of marine animals contain iron. The red corals contain 1% peroxide, which appears to be a colouring principle.\* Herberger found in *Spongia usta* 8.6% protoxide of iron. The scales from the exterior of oyster-shells I found to contain, besides carbonate of lime and organic matter, 0.61% peroxide of iron, with some oxide of manganese, and 0.15% carbonate of magnesia. Although these quantities of iron may be separated by organic agency, it is nevertheless impossible to suppose that the considerable quantities of carbonate of iron found in some grau-wacke limestones have a similar origin.† Here again the conjecture suggests itself, that this proto-carbonate of iron is derived from sea-water by the displacement of a corresponding quantity of carbonate of lime. This is the more conceivable, as in many marine-shells, iron ochre, brown iron ore, and even iron glance, have displaced the carbonate of lime.‡

R. Ludwig holds it as probable, since almost every clayey sphærosiderite in the coal-formations contains impressions of algæ and ferns, that these destroyed plants have effected the separation of the carbonate of lime, which was, according to my view, subsequently displaced by the carbonate of protoxide of iron contained in the waters.

The occurrence of quartz, chalcedony, semiopal, hornstone, cornelian, &c., in the form of calc-spar, proves that silica is capable of displacing carbonate of lime. Silica frequently occurs as the petrifying material of organic remains, having displaced the calca-

\* A. Vogel, in Schweigger's Journ. Vol. 18, p. 146.

† Von der Marck found as much as 15.9 per cent. carbonate of iron in Westphalian grau-wacke limestone.

‡ In the ferruginous sand of the chalk formation at Woodstock, in New Jersey, the *Gryphæa convexa*, Say, does not unfrequently occur, petrified by iron ochre. Blum erster Nachtrag, p. 206; also Bronn's Handb. einer Gesch. der Natur. Vol. 2, p. 713.



reous substance. In ordinary flint, the carbonate of lime is displaced by silica. Traces of streaks and planes of stratification traverse uninterruptedly the siliceous concretions; which appears to show that they were not formed until after the surrounding limestone, with its fossil remains, had been deposited and stratified. From all these facts it follows, that siliceous formations originated in the sedimentary limestones after their formation.

Although silica is separated directly from sea-water by organic agency (p. 184), still this separation may also take place in consequence of a displacement of the sedimentary carbonate of lime and the animal remains contained in it. When the carbonate of lime acts as the precipitant to carbonates of magnesia, protoxide of iron, and silica, in sea-water, equivalent quantities of it enter into solution again. Thus it is not only on the land that we find carbonate of lime subject to a continual alteration of solution and precipitation, but equally so in the sea.

But all these actions coincide in preventing the accumulation of the earthy carbonates, proto-carbonate of iron, and silicic acid, which would cause the sea to be uninhabited, whereas it is destined to accommodate a greater abundance of animal life than the continent. The effect assumes the character of cause; for it was reserved for animal life to restore the equilibrium. Constituents of sea-water become the coverings, the dwellings, of the minutest animals; after their death, they return again into the mineral kingdom, whence they originated.

If we remember that these microscopic organisms are uninterruptedly active near the poles, as well as in the depths of the sea, which exceed the height of our loftiest mountains, in mines,\* as well as in fossil strata,† where water alone appears to provide an atmosphere, it may then be possible to form some conception of the share which they take in the formative processes of the mineral kingdom.

While the roots of plants are the ever active collectors of alkalies, lime, magnesia, sulphur, phosphoric acid, &c.; while the fuci absorb the iodine, which constitutes less than a millionth of sea-water; so the marine animals are not less actively the collectors of carbonate of lime, silica, phosphoric acid, iodine, &c. The smallest of these animals are those extensive collectors (exten-

\* In the Freyberg mine, Bescheert-Glück, the *Gallionella ferruginea* lives frequently at a depth of 1100 feet.

† The Berlin infusorial strata may be traced to a depth of 100 feet, and it is by no means destitute of life, but is much rather in a condition which proves the power of propagation of great masses of individuals.

sive by their numbers) which, after their death, constitute thick beds which, when at a subsequent period they are elevated from the sea, extend over entire lands.

I think the plutonists might be induced, by the fact of the colossal creations of the infusoria, to direct their researches to the immediate neighbourhood of these creatures, and see whether it might not be possible there to find what they vainly seek in unknown depths.

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## CHAPTER X.

### THE ATMOSPHERE.

ATMOSPHERIC air is not only necessary to the existence of plants and animals, and of important influence in decomposing their dead substance; its constituents are likewise the principal causes of the disintegration of rocks.

Assuming the physical and chemical characters of atmospheric air to be known, I shall here consider only the processes by which the quantitative relation of its constituents is subjected to perpetual alteration, both now and ever since the most remote period.

The four essential constituents of atmospheric air—oxygen, nitrogen, carbonic acid, and aqueous vapour—are subject to constant variations, in consequence of processes going on upon the earth's surface; in the course of which, on the one hand, some of these constituents are abstracted, and on the other, fresh quantities of them are again supplied. From the immense mass of the entire atmospheric envelop, and its physical properties, it is easily conceivable that considerable quantities of one or other gas may either be abstracted from or introduced into it, without giving rise to any such change of quantitative relation as would be recognisable by chemical analysis.

The processes by which oxygen is continually abstracted from the atmosphere are :—

1. Animal respiration.
2. Decay of organic matter.
3. Combustion.
4. Oxidation of inorganic substances.

The elimination of oxygen from carbonic acid, and probably

from water, by the chlorophylle of plants under the influence of light, is the only means by which oxygen is supplied to the atmosphere. Vegetation constantly restores a quantity equivalent to that which is consumed by the respiration of animals and the decay of organic matter.

This constant circulation takes place during periods of variable duration. A great part of the carbon and hydrogen in the annual plants and fruits consumed as food by men and animals, is immediately restored to the atmosphere in the state of carbonic acid and water. The carbon, assimilated by perennial plants, does not again pass into the atmosphere until after long periods, and that, buried in the sedimentary strata in the form of coal, has been removed beyond the range of this circulation for inconceivable ages. Were not this carbon brought to the surface by human industry, and again restored to the atmosphere by combustion, it would perhaps be questionable whether this carbon would ever again return to it, since carbon is one of the substances least subject to change.

The uninterrupted motion in the atmosphere is sufficient to explain the extremely minute variations in the relative proportion of oxygen and carbonic acid, even although during certain seasons of the year the decomposition of the latter is entirely suspended in some regions.

Besides those universal means by which carbonic acid is supplied to the atmosphere—respiration, combustion, and various processes of art—we must notice :—

1. Exhalations of carbonic acid, which ascend from unknown depths into the atmosphere.

2. The deoxidation of mineral substances, especially peroxide of iron and sulphates, by carbonaceous substances.

Liebig\* considers that the 2,800 billion pounds of carbon which the present atmosphere contains in the state of carbonic acid, amounts to more than the weight of all the plants and of the known coal-beds upon the whole earth. If this quantity were distributed over the earth's surface, it would form a layer of only 0.962 line in thickness. It is evident that this is far short of being equivalent to all the carbon of the organic kingdom, belonging either to the existing or to the previous states of the earth; for we must take into account, not only the carbon of vegetable and animal remains, and of the coal-beds, but also that of the bituminous substances with which all sedimentary strata are impregnated, and which we have no means of estimating with accuracy.

\* Die Chemie in ihrer Anwendung auf Agricultur, &c., p. 22.

Assuming that all the oxygen in our atmosphere has been derived only from the decomposition of carbonic acid, the carbon thus separated would be sufficient to form a stratum, covering the entire surface of the earth, 2·3 feet in thickness. This thickness would be lessened by an aliquot part, if a portion of the now existing oxygen of the atmosphere should have been derived from water decomposed by the process of vegetation. If, on the other hand, a part of the oxygen of the former atmosphere should have been permanently lost to the present atmosphere, the thickness of the stratum of carbon would be increased by an aliquot part.

I consider that I have discovered a very considerable cause of diminution of atmospheric oxygen in the peroxidation of iron and manganese in rocks during their disintegration.\* At the time when I wrote, it was already known that decaying organic substances reduce peroxide of iron to protoxide (p. 166). But it was not until later, upon further investigation, that I ascertained this to be a universal process in sedimentary rocks. There is no doubt that the suspended particles from which these strata were formed, and which were conveyed to the sea by rivers, as well as those which are now similarly conveyed, contained iron for the most part in the form of hydrated peroxide. Thus a partial deoxidation must have taken place upon the bottom of the sea, and this can only have been effected at the cost of dead organic matter, the former presence of which is proved by the fossil remains in sedimentary strata. The proto-silicates of iron, which exist in the greenish clay-slates in larger quantities than the persilicates, therefore owe their origin to this reduction. Inasmuch as this reduction was effected by the carbon of organic remains, carbonic acid was formed; and through the decomposition of this, by plants, the oxygen abstracted from the atmosphere by protoxide of iron, during the decomposition of rocks, was again restored. The formation of iron pyrites from sulphates, peroxide of iron, and organic matter, likewise restored carbonic acid to the atmosphere (p. 163), to be again decomposed by plants.

There appears, consequently, to be a continual circulation of the oxygen. That abstracted from the atmosphere by various processes of oxidation is again returned to it after periods of greater or less duration. That part only which converts the protoxide of manganese of rocks into peroxide, appears to be permanently lost, for it is only in rare cases that this can again be restored by processes of reduction. On the other hand, the oxygen restored to

\* Bischof, German Edition. Vol. ii, p. 33.



the atmosphere in the form of carbonic acid during the formation of iron pyrites, originates in the mineral kingdom. If this carbonic acid be decomposed by vegetation, the atmosphere receives a quantity of oxygen which never before belonged to it. This is, at least, in the highest degree probable as regards the oxygen thus derived from protoxide of iron, for there is nothing to justify the opinion that metallic oxides have been formed from metals. If, moreover, other sulphurets have also been produced by a similar chemical reaction of sulphates and metallic oxides at the cost of organic remains, a still greater quantity of oxygen would by this means have been conveyed to the atmosphere, which never before belonged to it.

These facts show that carbon plays, as it were, the part of a carrier to the oxygen in the mineral kingdom. The carbon of organic substances, which now reduces sulphates, and is converted into carbonic acid, already existed at an earlier period in this form. Being then decomposed by the process of vegetation, the carbon was transferred to the organic kingdom; and if in this state it came in contact with sulphates, decomposition ensued, the carbon being again restored to the atmosphere as carbonic acid, to serve as food for plants. We may thus conceive that the same quantity of carbon may repeatedly transfer oxygen from the mineral kingdom to the atmosphere.

Oxygen is introduced into the atmosphere in a similar manner, by various industrial processes. In smelting-works, for instance, where oxides of iron are reduced by coal, the carbonic acid thus formed mixes with the atmosphere, and is decomposed by plants. Still this is merely a circulation; for the iron produced, gradually rusts, and again abstracts from the atmosphere as much oxygen as the reduction of its oxide had previously furnished to it. During a long series of years, coal remained untouched in the earth. The quantity which, since the first working of coal-mines, has been brought to the surface, is very considerable; and even if the quantity of carbonic acid formed by their combustion appears to be insignificant in comparison either with the quantity already existing in the atmosphere or that furnished by exhalations, it is still evident that, since the coal-beds have been worked, either the quantity of atmospheric carbonic acid must have increased, or, if this has been prevented by a proportionate increase of vegetation, the quantity of oxygen must have increased. Can this increase, either of carbonic acid or oxygen, occasioned by industrial operations, have been attended with any greater activity of those pro-

cesses in which these gases are consumed, namely, disintegration of rocks? It may well be imagined that increasing decomposition of rocks, and an augmenting vegetation, would advance simultaneously.

Although nature evinces an unmistakable tendency towards equilibrium, still it cannot be assumed that she conducts these processes as if by the balance. Processes which extend over long periods of time may therefore bring about a constant decrease or increase of one or other of the constituents of the atmosphere. The quantity of oxygen which the atmosphere contains amounts to more than two trillion pounds. A constant increase or decrease of atmospheric oxygen cannot therefore be recognisable until after long periods. Historical periods are lost in comparison with geological periods. The analysis of atmospheric air, even when made at very great intervals, would scarcely be capable of indicating such changes. Moreover, it is only during the last few years that this analysis has reached such a degree of accuracy that slight changes in the quantity of oxygen can be detected. The comparison of the examination of atmospheric air, made by Biot and Arago, 50 years ago, with another executed in the same manner 40 years afterwards, is the only evidence indicative of an insignificant change in the relative quantity of oxygen in the atmosphere.

Without taking into consideration the coal-beds which are sometimes several hundred feet in thickness, and undoubtedly exist in many places where they are not at all suspected, the carbon distributed throughout the sedimentary formations, as bitumen, &c., certainly amounts to a considerable quantity. If we consider the thick strata of black slate, saturated with carbon, occurring both in clay-slate and in the more recent schistose formations, the assumption of 0.1% as the average quantity of carbon present in rocks is certainly far short of the real amount.\* If, now, we assume the thickness of the entire sedimentary formations to be eight English miles, this quantity of carbon alone would equal a stratum 46 feet thick. The quantity of this carbon alone would be 20 times as great as that which the atmosphere would have furnished if all the oxygen now existing in it were the residue of decomposed carbonic acid, and 6,620 times as much as the actual quantity of carbon in the atmosphere, which Liebig assumes to be

\* The Silurian strata of the Scandinavian peninsula and the island Bornholm, contain, in their most ancient parts, considerable beds of alum-slate. In some districts of Westergothland, in Sweden, small beds of actual coal are sometimes met with. The alum-slate of Bornholm contains, according to Forchhammer, 8.65 per cent. of carbon.

an equivalent for all the carbon on the earth. The carbon which the atmosphere would have furnished, according to the above supposition, is therefore only a small part of all the carbon on the earth.

In Chapter XII, it will be shown that immense quantities of carbonic acid are continually poured out from the interior of the earth into the atmosphere. How long this phenomenon has continued we do not know. But, since the appearance of organic life upon the earth, we can conceive an application of this carbonic acid in the general economy of nature. As at the present time, by the decomposition of crystalline rocks, lavas, &c., which contain very little, or not a trace of carbon, productive soils are formed as soon as vegetation commences upon them, so it happened at the first commencement of vegetable life. The carbonic acid thus exhaled was decomposed by plants, and its carbon transferred to the organic kingdom, in which it partially remained after decomposition of organic bodies. The circulation thus commenced, became more general as vegetation continued to spread over the earth's surface, and increasing quantities of carbon were transferred from the atmospheric carbonic acid to the organic kingdom. A great deal of this carbon was restored to the atmosphere by decay of organic bodies; the residue remained in the sedimentary formation, until brought to the surface, by human industry, and again introduced into the atmosphere as carbonic acid by combustion. The incalculable quantities of carbon in the existing organized world, and their remains buried in sedimentary strata, which exceed the quantity of carbon in our present atmosphere by at least several thousand times, have therefore gradually passed from the interior of the earth through the atmosphere into their present store-houses, without any accumulation injurious to organic life ever having taken place.

While the carbon of the exhalations of carbonic acid gas was being transferred into the organic kingdom, into vegetable earth and sedimentary strata, the oxygen was transferred to the atmosphere, replacing that abstracted by the oxidation of mineral substances. This latter portion of oxygen, also, was subsequently restored to the atmosphere by the above-mentioned process of reduction, while new quantities of atmospheric oxygen were absorbed by the decompositions continually going on in rocks. It is superfluous to remark, that all these processes of reduction and oxidation take place uninterruptedly also at the present time.

This hypothesis is not inconsistent with any known facts, and is in perfect accordance with all that our short-sighted understanding can comprehend. It admits of our conceiving the possibility

that, since the appearance of organic life upon our globe, no essential alteration in the atmosphere has taken place, and that at the commencement of this long period, as well as at the present time, the conditions for the development of every organic species were present in the medium which surrounds the earth. If, however, the history of the vegetable and animal kingdoms, and especially of the organic remains imbedded in the sedimentary strata, is considered to afford a testimony to a progressive succession of organisms,—the disappearance of one species, and the development of another,—then adopting the above hypothesis, it will at least not be necessary to seek the cause of these changes in a variability of the atmosphere, but in other determining circumstances, perhaps in the decreasing temperature of the earth's surface. But all the carbonic acid which is evolved from the interior of the earth, is not decomposed by plants, for a part of it is consumed in the decomposition of the silicates of lime, protoxide of iron, alkalies, &c., in rocks, and their conversion into carbonates. This gas thus finds a double application. The one part, which combines with lime and other bases, returns undecomposed into the mineral kingdom; the other part is decomposed by plants, and its constituents divided between the mineral and the organic kingdoms. If we glance at our massive sedimentary limestone rocks, one of these decomposition products meets our view upon a gigantic scale.

Stratified formations, destitute of organic remains, would seem to be an evidence that they were deposited at a period previous to the appearance of organic life. But sedimentary strata being the final product of mechanical disintegration and chemical decomposition, we must necessarily assume the pre-existence of the substances principally active in causing these changes, viz., carbonic acid and oxygen. If at that period no vegetation existed, the relation between these atmospheric constituents, and the rocks on the surface of the earth, must have been essentially different from that which has obtained since the commencement of the organic period. They would, indeed, both have acted as decomposing agents upon rocks; but the carbonic acid would not have been decomposed, and consequently, the oxygen would not have been renewed. If, therefore, there were at that time exhalations of carbonic acid, they might have continually replaced that which was abstracted in the formation of carbonates; but processes of deoxidation could not have taken place, because of the absence of decaying organic remains. Therefore, the oxygen which combined with protoxide of iron was lost to the then existing atmosphere; and this leads to



the assumption, that it must, in the primitive period of the earth's existence, have contained more oxygen than at the time of the appearance of organic beings.

Whether, moreover, the formations designated as lower stratified or non-fossiliferous rocks do really belong to the period anterior to the existence of vegetation, is to be doubted. The colour of the dark-blue, and sometimes quite black clay-slate, in which no fossil remains are found, is owing to the presence of carbon disseminated throughout the whole mass. If all carbon originates in decomposed carbonic acid, then the formation of this clay-slate must have been subsequent to the appearance of vegetation, and so far the existence of organic life would extend beyond the period of *grauwacke* formations.

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## CHAPTER XI.

### NITROGEN AND ITS COMPOUNDS.

AMONG the few simple substances which we find upon our earth and in the atmosphere, nitrogen is certainly among the primitive. No other simple substance occurs in so large a quantity. While we can easily recognize the absolute indispensability of the other constituents of the atmosphere for the economy of nature, it would be difficult to demonstrate the particular office of the very much greater quantity of nitrogen. Nevertheless, the conjecture that this gas is the source of all nitrogenous compounds, is far from improbable. The nitrogen which is evolved from springs, is derived either from the atmosphere or from the decomposition of nitrogenous organic remains in sedimentary strata. All kinds of water which come in contact with the atmosphere, take up quantities of its constituents, varying according to their unequal solubility. In all cases these waters absorb least nitrogen. A combination of this absorbed nitrogen with other constituents of these waters, or with substances with which they come in contact in their subterranean course, is inconsistent with the known chemical behaviour of this gas. Consequently, the entire quantity of nitrogen thus absorbed, is retained so long as the pressure or the temperature does not alter. On the contrary, the oxygen and carbonic acid absorbed by water, enter into combination with mineral substances, and these gases disappear as such.

If the pressure decrease, or if the temperature of the circulating water rise, the absorbed nitrogen escapes. If all the oxygen has not been consumed, more or less of it is also evolved.

In fissured rocks, water is abundantly brought into contact with atmospheric air and absorption is thus favoured. If, moreover, a powerful hydrostatic pressure is also in action, more atmospheric air is absorbed than under ordinary circumstances. The crevices and hollows, which are filled during the wet seasons, are again partially emptied during dry weather, and atmospheric air again gains admittance. By means of this change of the water in subterranean channels, a constant renewal of the absorbed air is effected. If such water rises as a spring, it is a necessary consequence that, with decreasing hydrostatic pressure, the gases absorbed should separate and rise in the water as bubbles.

When meteoric water, holding in solution the gases absorbed upon the surface of the earth, penetrates to deeper, and consequently warmer strata, and then rises again in warm springs, these gases are evolved more readily. Thus, although the numerous cold springs in Paderborn evolve little or no gas, the quantity is greater in proportion as their temperature is higher. In the warmest ( $56^{\circ}$  to  $61^{\circ}$  F.) bubbles of gas rise almost uninterruptedly, consisting of 87 nitrogen and 13 oxygen.\*

The warm sulphur springs very frequently exhale nitrogen without oxygen, which is partially owing to the circumstance that the latter cannot remain in a free state together with sulphuretted hydrogen. But it is by no means to be supposed that nitrogen is in all cases derived solely from the atmosphere. In the putrefaction of nitrogenous organic substances under water, nitrogen is always liberated. The nitrogen exhaled from warm springs containing nitrogenous organic substances, undoubtedly originates in this way. It is also possible that the formation of these substances may be connected with a separation of nitrogen.

Nitrogen is likewise found among the gases which are exhaled during volcanic eruptions. In this instance also, it must be derived either from the atmosphere or from the decomposition of organic substances. The water, whether of meteoric, spring, or oceanic origin, which penetrates to the volcanic foci, contains atmospheric air. When this water is afterwards exhaled in the form of vapour, the gases which it contained are carried with it. The oxygen may be partly consumed in the oxidation of combustible substances, such as sulphur, and the nitrogen alone be evolved. If the water

\* Bischof, neues Jahrbuch der Chemie und Physik, Vol. 8, p. 257, et seq.

which penetrates to the volcanic foci contains, besides atmospheric nitrogen, nitrogenous substances, as for instance, sea-water, these would also yield nitrogen, in consequence of the decomposing action of heat. Volcanos whose craters, like that of Vesuvius, are situated in sedimentary formations, exhale nitrogen derived from the decomposition of the organic remains of these strata.

There is no single phenomenon which can justify the assumption of the existence of unknown compounds of nitrogen, or even of uncombined nitrogen, in the interior of the earth. All exhalations of nitrogen originate either in the atmosphere, or in the decomposition of organic remains.

Among all the combinations into which nitrogen enters with the other elementary substances, nitric acid is the only one which can be formed directly. It is known that if a succession of electric sparks be passed through a mixture of oxygen and nitrogen, nitric acid is formed, and indeed it is found in the rain which accompanies a thunder-storm. This is, moreover, the only known process by which nitric acid is generated in nature.

The formation of nitrates on sedimentary rocks (limestone, marl, sandstone) and in alluvial strata, presupposes the presence of nitrogenous organic remains. Heat favours putrefaction, and consequently the formation of nitrates, and it is on this account that we find nitrates produced, especially in southern countries; as, for example, in France, Spain, Italy, in the East Indies in very large quantities, in Persia, China, Egypt, America, &c. John Davy\* found the rocks of the cavern of Ouva, to contain  $26\cdot7\frac{9}{10}$  animal matter, and other rocks only traces.

Liebig† is of opinion that, owing to the presence of ammonia in the atmosphere, nitrates may be formed in materials which do not contain any nitrogenous substances, since most porous bodies condense ammonia largely. Schönbein‡ believes it may be assumed that, in the decay of nitrogenous organic substances, ozone is eliminated, and that it is this agent which directly converts their nitrogen into nitric acid.

According as the rock, in which the decay of organic remains takes place, contains either potash or soda, the nitrate of one or other of these bases is formed; thus, nitrate of soda is found in abundance in Peru, and near Iquique in Chili.§ Where alkalies

\* *Annal. de Chim. et de Phys.* Vol. 25, p. 209.

† *Agricultur-Chemie*, p. 263.

‡ *Poggendorff's Annal.* Vol. 67, p. 216.

§ *Darwin's Naturwissenschaftliche Reisen.* German edition, Vol. 2, p. 136.

are absent, nitrate of lime is formed, which is found as an efflorescence upon walls and in limestone caves, as well as in some districts of Africa and Spain.

Ammonia, as well as nitric acid, is a product of the decomposition of organic remains, the former not only by putrefaction, but also by the action of heat. It has not hitherto been possible to effect a direct combination of nitrogen with hydrogen. As early as the year 1804, Th. de Saussure found that a solution of sulphate of alumina exposed to the air was converted into ammonia alum. Liebig\* proved by direct experiment the presence of ammonia in the atmosphere. Græger† found the quantity in 36 cubic feet of air to be 0.4575 milligramme. According to Ville,‡ however, the quantity of ammonia contained in the air is scarcely estimable, when all accidental exhalations are avoided. Liebig and Boussingault assume that ammonia existed in the atmosphere before the appearance of organic life:§ this assumption is certainly incorrect.

The ammonia contained in iron ores, and in hydrated oxide of iron formed by the oxidation of iron in the air, as well as the ammonia which, according to Faraday's experiments, is obtained by igniting potash with substances free from nitrogen, is regarded by Liebig|| as being derived from the atmosphere. The ammonia of the aqueous vapours in the Suffioni of Tuscany is considered by Liebig¶ not to originate from animal organisms, but to have existed prior to all life. As opposed to this view, it must be remembered that these exhalations come from sedimentary limestone, which always contains organic remains. From the great inclination of these strata, it may be inferred that they extend to considerable depths. Boring experiments have been made near the Lago di Monte Rotondo, by means of which a temperature equal to that of boiling water was reached, at a depth of only 45 to 60 feet, and streams of aqueous vapour burst forth with irresistible force.\*\* Nothing can, therefore, be more readily con-

\* Loc. cit., p. 56.

† Archiv. der Pharmacie. Vol. 44, p. 35.

‡ Comptes rendus. Vol. 31, p. 578.

§ Journ. für pract. Chemie. Vol. 3, p. 160.

|| Loc. cit., p. 282, et seq. During the rusting of iron, a small quantity of ammonia may be formed directly at the cost of water; for, according to the experiments of my son, Dr. Ch. Bischof, iron filings under water disengage hydrogen, and it is very probable that in such a gradual elimination of hydrogen, it may enter into combination with atmospheric nitrogen.

¶ Loc. cit. p. 102.

\*\* Bunsen, in the Annal. der Chemie u. Pharm. Vol. 49, p. 267.



ceived, than that even at such slight depths ammonia may be evolved from organic remains.

Even if no organic remains were present in the strata from which the Suffioni rise, still water, whether it comes from the surface of the earth or from the sea, always contains organic matter. Since, finally, crystalline rocks also contain organic matter, aqueous vapour at the boiling temperature would find even there material for the formation of ammonia.

Hot springs likewise, and especially sulphurous waters, contain materials for the formation of ammonia in the so-called baregin. The thermal springs of Aix-la-Chapelle and the Euganean mountains are a sufficient example of the large quantities of this nitrogenous substance which are brought to the surface. It is not probable that this substance is taken up by water, during its filtration through vegetable mould; for in that case we ought to find it in equal quantity in the water of cold springs. It is much more probable that water penetrating to great depths, and there becoming heated, extracts it from sedimentary strata saturated with organic matter. If, moreover, it is remembered that sulphurous waters originate in the mutual decomposition of sulphates and organic matter, it will appear highly probable that baregin is also a product of a similar decomposition, and does not exist ready formed in sedimentary strata.

Chloride of ammonium appears to have been deposited with chloride of sodium from cold water. At least, A. Vogel\* obtained it by sublimation from the salt of Friedrichshall, Rosenheim, Kissingen, Oeb, and Dürkheim, as well as from the rock-salt of Hall in the Tyrol; and Heine† detected it in the mother-liquor of the salt-pans at Halle.

If all these facts are considered, it will be impossible to ascribe the aqueous vapours of the Suffioni to primitive water, which never came into contact with living organisms. Moreover, Payen speaks decisively of organic matter, an *odeur de marée* in the condensable products of the vapour.

The presence of ammonia in iron ores is more readily explicable; for they, like all other ores, being deposits from water, this ammonia originates in organic matter contained in the water from which these ores were deposited. We cannot, indeed, be surprised that the hydrated oxide of iron which we find in volcanic rocks, should contain ammonia; for this oxide has

\* Journ. für pract. Chemie. Vol. 2, p. 290.

† Karsten's and v. Dechen's Archiv. Vol. 19, p. 25.

originated in the decomposition of minerals containing proto-silicates of iron, by means of water which has penetrated from the surface and deposited a part of the organic matter held in solution.

Even if ammonia should be detected in the iron glance occurring in the crater of Vesuvius, it would be no proof of the primitive existence of ammonia. Chloride of ammonium is found in the ejections of this volcano. During the eruption of 1794, the quantity of this salt was so great that the peasants collected it by hundred-weights. Thus the presence of ammonia in Vesuvius being indisputably proved, it could not be surprising if it were found there in combination with peroxide of iron. As the crater is situated in sedimentary limestone, it seems probable that the source of the ammonia should be sought in the organic remains of these strata. Aggregated fragments of limestone and lava are frequently found among the ejections.

During the last eruption of Hecla, September 1845, chloride of ammonium occurred in such quantities that it was found worth collecting. Bunsen\* proved by his own observations, and the testimony of credible witnesses living in the island, that this sublimation of chloride of ammonium did not extend beyond where the ground covered with vegetation was overflowed by lava. The erroneous assumption of Waltershausen† that this ammoniacal salt was produced at the cost of atmospheric air, was disproved.

Even when the crater and the channel of a volcano are not situated in sedimentary strata, but a communication with the sea exists, so that the evolution of vapour originates in sea-water, the organic remains of the latter furnish adequate material for the formation of chloride of ammonium. In all volcanoes situated near the sea, there is then a near source of this salt. Thus, according to Breislak, it appears to be always present in the vapours of the Solfatara at Puzzuoli. It is likewise met with, mixed with sulphur, on the island of Vulcano. According to Ferrara,‡ it is sometimes found in such considerable quantity at Ætna, that a very profitable trade has been carried on in it. It was also found upon the lava-streams at Laucèrole, formed during the eruption of 1824. It is thrown out in enormous quantities from the volcanoes of Ho-t-scheou or volcano of Turfan, and of Pe-Schan or volcano of

\* Compt. rend. Vol. 23, 1846 ; Ann. der Chim. u. Pharm. Vol. 65, p. 73.

† Physich-Geograph. Skizze von Island. 1847, p. 115.

‡ Ferrara, Campi flegr. p. 286.

Kutsché, in Central Asia. It is there collected, and is an article of commerce throughout Asia. Vapours of chloride of ammonium also occur between Samarkand and Farghara, &c. All that we know of these volcanoes has been collected by Humboldt\* from the accounts of various travellers. The distance of Pe-Schan from any sea is between 1,200 and 1,600 English miles; but the lake Temurtu or Issikul, which is from 68 to 72 English miles long, and from 24 to 28 broad, and appears to contain warm, salt, and ferruginous water, is only 100 or 180 miles distant. From these statements, although imperfect, it would seem to follow, that the chloride of ammonium vapour is accompanied by aqueous vapour. But if such be the case, it is to be inferred, either that salt water containing organic substances penetrates to the volcanic focus and is there converted into vapour, or that the vapour originates in sedimentary strata impregnated with organic matter to which salt water has access.

There is, then, nothing to justify the assumption that ammonia can be formed by the direct combination of its constituents in any volcano. Even the favourite and so frequently misused theory of the influence of pressure, cannot afford any support to this assumption; for it is known that hydrogen and nitrogen do not combine, at ordinary temperatures, under a pressure of even 50 atmospheres. Those who are inclined to assume that the combination may take place at higher temperatures, must not forget that ammonia is decomposed at a red heat.

The sublimation of chloride of ammonium by subterranean fires, shows, in a striking manner, what really takes place when water comes in contact with rocks containing organic remains at a high temperature. Hot aqueous vapour and hot air are continually evolved from fissures in the shale, at the so-called Brennenden Berg of Duttweiler, near Saarbrücken; and crystals of chloride of ammonium are frequently deposited. This evolution of vapour presupposes a continual access of water to the heated rock. Probably this water furnishes the chloride of sodium and other chlorides necessary for the conversion of the ammonia formed from the organic remains in coal or slate-clay, into chloride of ammonium. These are processes which we can without difficulty imagine to take place in the volcanic foci of Asia. Chloride of ammonium is also found at other places, as a

\* Poggend. Annal. Vol. 18, p. 332, et seq.

sublimate arising from the combustion of coal strata; for instance, at St. Etienne, near Lyons,\* at Newcastle and at Glan in Rhenish Bavaria.

It follows from the above considerations, that the only condition under which it is known that a nitrogenous compound is formed directly in the absence of organic matter, and which can be regarded as actually obtaining in nature, is that already spoken of as determining the formation of nitric acid, viz., the influence of electricity upon atmospheric air. Of 77 quantities of rain-water collected and analyzed at different times, Liebig† found that 17, collected during thunder-storms, contained more or less nitric acid combined with lime and ammonia. Of the remaining 60, only two contained traces of nitric acid.

If it be considered that this formation of nitric acid has gone on uniformly as long as the present meteorological relations have existed, it may easily be conceived that the total quantity which has been thus formed up to the present time must have been very considerable. The nitric acid formed in the atmosphere was, in remote times, as at present, conveyed to the surface of the earth by rain, where it partly contributed to the decomposition of rocks, and partly combined with the saline bases dissolved in sea-water. The nitrates formed must, in both cases, have accumulated in the sea. The question then arises, whether these nitrates yield nitrogen to land as well as marine plants? Kuhlmann‡ found that nitrate of soda, as well as ammoniacal salts, acted as manures. The experiments of Boussingault,§ Barclay, and Gourcy, have added additional evidence in favour of the increased production of vegetable substance, in consequence of the use of nitrate of soda.

Hitherto chemical analysis has not indicated the presence of nitrates in rock-salt, which is undoubtedly a marine deposit. Neither could Heine|| detect nitric acid in the salt-brines of Prussian Saxony. There can, however, be no doubt that the waters of the ocean receive a constant supply of nitrates, and have continued to do so ever since its existence. It therefore naturally suggests itself, that these substances, which are either wanting in sea-water, or can be recognised only in very minute quantities,

\* *Annal. de Chim. et de Phys.* Vol. 21, p. 158.

† *Loc. cit.*, p. 298.

‡ *Comptes rendus.* 1843. Vol. 17, No. 20, p. 1118.

§ *Rural Economy.*

|| *Karsten's and v. Dechen's Archiv. &c.* Vol. 19, p. 27.



should be sought for in the nitrous constituents of plants and animals which have been produced and have died in the sea, and whose remains, buried in the sedimentary mud, have been removed, and are still being removed, from the general circulation.

Assuming that Græger's analysis (p. 210) gives the true quantity of ammonia in the atmosphere, it follows then, that an atmospheric column having a basis of one square foot contains 4.76 grains. Supposing this quantity of ammonia to be in the form of a liquid of the density of water, it would form a layer of 0.135 line in height. Now, 4.76 grains of ammonia contain 3.921 grains of nitrogen, and this then is the entire quantity which the plants growing upon a square foot of surface could assimilate if they abstracted the whole ammonia from the superincumbent atmospheric column. According to Chevandier,\* the proportion of carbon relatively to nitrogen in beech-wood is as 1800 : 34; according to Liebig, a square foot of land produces annually  $\frac{1}{4}$  lb. of carbon; consequently, the beech-wood growing upon this surface requires annually 3.627 grains of nitrogen. This is nearly as much as the quantity of nitrogen, present in the form of ammonia, in the superincumbent atmospheric column. Accordingly a beech forest consumes in 13 months all the ammonia contained in the atmospheric column resting above it. This ammonia would, therefore, long since have been consumed, if the vegetation of forests, frequently continuing for a century, or even more, had gone on merely at the cost of atmospheric ammonia.

In a country in which  $\frac{5}{6}$  of the surface was forest, and  $\frac{1}{6}$  arable land and meadows, the former would in 54 years absorb all the ammonia of the atmosphere resting upon the entire surface. In the second period of 54 years, the vegetation of the wood and that of the fields would share the ammonia in circulation between them, and consequently be scantily supplied. After this process had been repeated several times, the atmospheric ammonia would decrease to a minimum, and the vegetation would be constantly more scanty, and finally cease altogether.

I have found, by experiment,† that in the combustion of wood, by far the greater part of its nitrogen is separated in a free state; consequently only a very small proportion of ammonia can be introduced into the atmosphere by this means. And not only is nitrogen liberated in combustion, but even in putrefaction this is

\* Comtes rendus. 1844. Nos. 3 and 5.

† German edition. Vol. 2, p. 132.

effected, though in a less proportion, as has been already remarked (p. 208).

The combustible gas evolved during the progressive decomposition of coal, is always accompanied by nitrogen. According to my examination of three such exhalations, the quantities of nitrogen amounted respectively to 2, 5, and 15 $\frac{0}{100}$ . This gas is evolved under pressure, and contains no oxygen; therefore the nitrogen cannot be derived from the atmosphere, but must have the same origin as the accompanying combustible gas, namely, from coal. Nitrogen is likewise mixed with the combustible gas evolved by putrefying organic substances, in marshes and standing water. Hence it may be inferred, that this liberation of nitrogen accompanies the decomposition of nitrogenous organic matter from the first to the last stage. Therefore the nitrogenous substances of the plants which have furnished the material for the coal-beds, do not again return as such into circulation. After their complete decomposition, however, their nitrogen passes into the atmosphere. The ammonia introduced into the atmosphere by the combustion of coal, certainly cannot be equivalent to more than a very small fraction of the nitrogen in the original substances. It is extremely probable that the vegetable substances which are converted into graphite, have given up all their nitrogen, as nitrogen gas, to the atmosphere.

Thus we see, that precisely the largest quantities of the nitrogenous organic substances which nature produced during the earliest of the organic periods, return to the atmosphere, not as ammonia, but as nitrogen. It therefore necessarily follows, that if all nitrogenous substances are not finally to disappear, new ones must be continually produced from the atmospheric nitrogen. Besides the formation of nitric acid in the atmosphere by electrical agency, there is also an organic process by which nitrogenous substances are produced. It can scarcely any longer admit of doubt that plants assimilate nitrogen directly from the atmosphere. Mulder\* has already proved this experimentally, and other chemists have confirmed it. Ville† found, moreover, that the atmospheric ammonia took no perceptible share in vegetation.

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\* Bulletin des Sciences ph. et nat. en Néerlande. 1840.

† Comptes rendus. Vol. 31, p. 578.

## CHAPTER XII.

## CARBONIC ACID EXHALATIONS.

As far as regards frequency of occurrence, these exhalations are the most important; they constitute one of the most stupendous of terrestrial phenomena, exercising both in past and present periods the most important influence upon the decomposition of rocks.

Carbonic acid is evolved from a numerous class of springs, which are abundantly distributed over the surface of the earth, especially in districts where extinct volcanoes or basaltic rocks occur. Carbonated springs, which evolve abundance of this gas, are likewise met with in the midst of sedimentary formations.

Carbonated springs are very numerous in Germany; they occur in the Eifel, in the neighbourhood of the Lake of Laach, and the Siebengebirge, in the Westerwald, the Taunus, Habichtswald, Meissner, Vogelsgebirge, the Rhone, Fichtelgebirge, Erzgebirge, the Bohemian Central Mountains, and the Riesengebirge, more or less numerous, and with varying exhalations of carbonic acid. They follow exactly the basalt, extending from the Eifel to the Riesengebirge.\*

In the Eifel and the Lake of Laach district there are certainly more than a thousand such springs, and not unfrequently a great number are crowded close together at one point. But the carbonic acid is evolved here, not only from the springs, but also directly from the ground, from the water of the streams and fissures of the rocks.

Since the year 1810, a spot upon the right bank of the Kyll river, near Birresborn, has been known under the name of Brudeldreis, where carbonic acid is evolved from a fissure in clay slate. Another exhalation occurs 10 miles from Treves, in the neighbourhood of Hetzerath, which is precisely similar to the above.† There can be no doubt that, by a closer investigation, many similar exhalations would be found not issuing directly from springs.

\* See the author's *Vulcanische Mineralquellen*. Bonn, 1826, p. 161—230.

† Nöggerath and Bischof, in the *Jahrbuch der Chemie u. Physik*, 1825, Vol. 12, p. 28.

But as they generally occur at low situations, which are covered by the water of adjoining brooks or rain-water, they are scarcely distinguishable from carbonated springs, and are generally considered to be such. Nevertheless, they differ from these in having no issue of water. When the water of the basin is drained off, or otherwise removed, gas alone issues, and no water. The absence of ferruginous deposits may also serve as a characteristic; for the waters of most carbonated springs, accompanied with abundant evolution of carbonic acid, are ferruginous, and deposit iron ochre upon the surface where they issue.

Besides the numerous carbonated springs in the neighbourhood of the Lake of Laach, there are also a great number of spots where carbonic acid is evolved from the ground. The valley which descends from Burgbrohl will serve as an example. Upon the mountain declivities there are here and there small depressions in which dead birds, mice, &c., are always found; and, on stooping down, the penetrating odour of carbonic acid is perceived. Upon the fields are patches where vegetation is very scanty, and the odour of carbonic acid is very distinct near the surface, especially in wet weather. Bubbles of gas escape uninterruptedly at many parts of the brooks; at one spot, where this evolution of gas was especially abundant, the owner of the land, supposing it to be due to the presence of a mineral spring, led the brook round by another course, in order to take advantage of it. The earth was dug out all round, to the depth of 12 or 15 feet, the hole becoming filled partly with spring-water and partly by the water of the brook. By this means, many channels were opened from which immense quantities of gas streamed out. Several cellars in the village of Burgbrohl are filled with carbonic acid gas to such an extent that they could not be entered; and in the excavation of new cellars the workmen were much troubled by the evolution of gas.

All these phenomena are repeated in other valleys near the Lake of Laach, and indeed more strikingly the deeper the valleys become. It is on this account that they are most prominent in the valley of Burgbrohl, which is the deepest of all. At the Lake of Laach, a few paces from the shore, is an exhalation of carbonic acid, which has long been known.

All these exhalations, however, originate from deeper carbonated springs; in no case can carbonic acid proceed from the original focus of its evolution without meeting with water. The circumstance that the temperature of such exhalations is,



according to numerous observations which I have made, always very near that of the adjoining carbonated springs, testifies to this.

Upon the eastern shore of the Lake of Laach bubbles of carbonic acid rise abundantly. A mile from the lake, near the village Wehr, the evolution of gas is remarkably great; here are innumerable springs close to one another, and as there is no discharge, they form a marsh of considerable extent. The hissing of the gas, which partly rises in bubbles several inches in diameter, and forces the water upwards to the height of more than a foot, is there so loud that it may be heard at a considerable distance. The deposits of iron ochre, which furnish material for industrial purposes (in no inconsiderable quantities\*), show what enormous quantities of carbonated water and carbonic acid must have issued from the earth at this place since a time inconceivably remote.

It is very probable that the circular valley in which these exhalations of carbonic acid occur, is the crater of an extinct volcano. If the Lake of Laach was also formerly a crater, then it and the valley of Wehr are the only two instances in which the evolution of carbonic acid presents itself in the extinct crater itself, for in the other more elevated and undoubted craters no such exhalations are found.

The exhalations in the neighbourhood of the Lake of Laach issue partly from alluvial land, trass, volcanic ashes, &c., partly from the clay-slate itself, which in that case is not very distant. It is highly probable that they all proceed from this rock. The focus of their formation is certainly not in the volcanic masses which cover it, but must be sought much deeper down.

At the foot of many volcanic cones between the Lake of Laach and the Moselle no exhalations are observed, with the exception of one near Frauenkirchen. But this district is covered with a very thick bed of pumice-stone, volcanic ashes, &c., which in many places lie upon the trass. In a more distant valley, however, as well as in the deep valleys which open into the valley of the Moselle, several mineral springs issue from the clay-slate, with a tolerably abundant evolution of carbonic acid.

In the Ahrthal, about eight miles north of the Lake of Laach, there is at the foot of the basaltic Lands-Krone a mineral spring with a somewhat considerable evolution of carbonic acid. In the neighbourhood of this and another basaltic hill (Neuenahr) copious exhalations of carbonic acid gas from acidulous springs were recently detected while sinking many pits. There is an

\* See the author's paper in Schweigger's Journ. Vol. 56, p. 146.

extensive district, all over which such quantities of this gas are already evolved, in depths some feet beneath the surface, as to prevent further sinking without ventilation. The scanty growing of the vines upon a hill in this spot led to the detection of these exhalations, for it was observed that the roots of these vines were destroyed by them. On examining this spot, I observed large patches upon the fields, like those in the valley of Burgbrohl, where vegetation was very scanty; there is, consequently, no doubt that in the former of these localities there are also exhalations of carbonic acid, which prevent the growth of plants. It is worthy of notice, that the temperature of the springs in the above-mentioned pits rises from  $68^{\circ}$  to  $82^{\circ}$  F., while the highest temperature observed in the springs in the environs of the Lake of Laach is only  $58^{\circ}$  F. At the present time, borings are being made in the Ahrthal, because it is to be supposed that the temperature of the acidulous springs may still considerably increase at moderate depths.

At the foot of the last basalt cone upon the left bank of the Rhine, crowned by the ruin Godesberg, about 16 English miles from the Lake of Laach, there is another mineral spring with a feeble evolution of gas. On the contrary, on the whole right bank of the Rhine (which, from Leubsdorf beyond Linz as far as the immediate vicinity of Bonn, is covered with such a number of basalt cones, and includes the group of the Siebengebirge, composed of various crystalline rocks), there is nowhere a mineral spring nor a trace of carbonic acid exhalations to be found. They are also equally absent in the characteristic crater of the Rodderberg, near Mehlem, opposite to the Siebengebirge, and at the foot of the neighbouring basalt cone, upon which stands the ruin Rolandseck, and in the adjoining valleys. This is the more striking, from the fact that carbonic acid appears at the foot of the small basalt cone, Godesberg, and especially as three miles below Bonn there is, at Roisdorf, upon the left bank of the Rhine, a spring very rich in mineral constituents, and with a considerable evolution of carbonic acid, issuing from the side of a range of hills belonging to the brown-coal formation. The Roisdorf spring is the last which occurs in the whole valley of the Rhine until it falls into the sea, and it concludes the numerous series of mineral springs and exhalations of carbonic acid, whose centre is in the neighbourhood of the Lake of Laach and the Eifel, and from thence branches out in different directions.

The first exhalations of carbonic acid upon the right bank of

the Rhine, above the Laach district, occur at Ems, upon the right bank of the Lahn, and at several places in the bed of this river itself.

In the Taunus district there are a great number of very considerable exhalations of carbonic acid. Among others, the bored brine-springs at Nauheim (p. 189), which rise in a column 4 inches thick to a height of 18 feet above the level of the boring, as a steaming and frothing pyramid, consisting of an intimate mixture of water and carbonic acid. Other exhalations of carbonic acid, which have long been celebrated, are the so-called Grotto del Cano, near Lake Agano, in the neighbourhood of Naples; the caves in a thick lava-stream which extends from Clermont to Rojat, in the Auvergne, among which the cave of Montjoly is the most famous;\* the so-called Puits de Neyrac, or Puits de la Poule, in Vivarais;† the exhalations at Latera and Sciacca, in Sicily, &c.

It may be assumed that all these exhalations are of very great antiquity, and undoubtedly existed prior to the historical period. But, besides these, there are ephemeral exhalations, the ordinary moffettes, which regularly appear at many places in the neighbourhood of Vesuvius, after every eruption. They frequently make their appearance a month after the eruption, exercising a very destructive influence upon vegetation and animal life, but ultimately disappear entirely.‡

The gaseous exhalations in the neighbourhood of the Lake of Laach, whether issuing from springs or not, have only a slight pressure equal to a column of water four or five inches high. This shows that the carbonic acid rising from fissures in the clay-slate becomes much dispersed in the beds of detritus. The gas, meeting with obstacles at one place, seeks a passage at another. In the Lake of Laach, where all the fissures are filled with water, the gas rises wherever the depth is least. Therefore, it is evolved most abundantly near the shore, and it is only where the depth is not greater than 20 feet that separate bubbles appear. I have in vain sought in all directions for ascending gas-bubbles at points of the lake which are deeper. When in Meinberg (Lippe Detmold), where a considerable quantity of carbonic acid issues from the springs, I inserted the Douche tube into a vessel about 14 inches high, filled with water, and found that the gas not only passed through the

\* Le Grand d'Aussy, *Voyage d'Auvergne*. 1788, p. 116.

† Steininger *die erloschenen Vulkane in Süd-Frankreich*. 1823. p. 82.

‡ Von Buch, *Geognostische Beobacht. auf. Reisen*. Vol. 2, p. 156.

water, but forced it upwards, like a fire-engine.\* The gas conducted to the bath-house through narrow tubes 100 feet long, is stated to be capable of overcoming the pressure of columns of water 6 or 8 feet in height.

The very large quantity of carbonic acid which issues from the boring at Neusalzwerk (p. 146), exerts a pressure equal to 9 inches of mercury, or more than 10 feet of water. This was, however, by no means the maximum pressure which I was then unable to measure.

Before this boring was made, there was no exhalation of carbonic acid to be found anywhere near. It is, therefore, the only channel from which the gas can escape; and this accounts for the high pressure. Here, then, the single channel between the interior and the surface of the earth, and from which the gas issues, has been opened artificially, and at Meinberg a similar one has been formed naturally in the Kenper.

In the several exhalations of carbonic acid, a variation in the quantity of the gas has been observed. This fact has given rise to considerable discussion, and has not unfrequently been mystified.†

I have at various times, during a whole year, had an opportunity of observing four carbonated springs issuing near Burgbrohl, with strong evolution of gas. The springs were carefully enclosed, covered in air-tight, and furnished with leaden tubes from 6 to 30 feet long, which conveyed the gas into a factory. When not in use, the tubes were bent on one side, and not further regarded. I frequently smelt at the mouths of these tubes, in order to detect, if possible, any casual alteration in the issue of the gas. During protracted dry weather no carbonic acid could be recognized, but after long rains I again observed a strong smell of the gas. This phenomenon depends upon the circumstance that, in wet weather, the escape of the gas through the ground is obstructed by its being saturated with water, and it consequently issues through the lead pipes, while in dry weather it finds numerous passages through the dry ground, and therefore cannot stream from the long pipes, where it would have to overcome its own pressure.‡

The gas evolved from a mineral water must be carefully distinguished from the gas which remains absorbed by the water. A mineral water which evolves carbonic acid must be saturated

\* Journ. für. pract. Chemie. Vol. 1, p. 325.

† German edition, Vol. 1, p. 253, et seq.

‡ Ibid., Vol. 1, p. 256, et seq.



with this gas. This saturation, however, is regulated by the temperature of the water and by the atmospheric pressure. When the pressure is great and the temperature low, more carbonic acid is held in absorption than in the opposite case.\* In stormy weather, when the barometer is low, more gas is evolved from the water of carbonated springs than in fine weather.

The influence of motion in the atmosphere upon the issue of the gas, manifests itself according as it is evolved from level plains or from hollows. In the broad valley of Wehr, in which are the most considerable gaseous exhalations of that district, there is no danger in standing even in the centre, if care be taken not to sink into the ground, which is undermined by the continual exhalation of gas. Although it might have been expected that a dense atmosphere of carbonic acid existed there, the smell of this gas is scarcely perceptible, except on stooping down. The gas diffuses itself at once into the atmosphere, and although its quantity is so great, it is inconsiderable when compared with that of the atmosphere. The slightest motion in the superincumbent atmosphere causes an immediate diffusion of the gas, independently of its greater density.

The result is, however, very different when the gas is evolved in hollows, cellars, or caves. Such places after a while become entirely filled with carbonic acid, in consequence of its greater density, and the motion of the atmosphere has then no influence upon it. That portion only which rises above the edge of the hollow diffuses into the atmosphere. If such holes are not deeper than the height of a man, they may be entered without danger. While the head is above the edge, the gas is scarcely smelt. But care must be taken in stooping for the purpose of detecting its presence; for by coming too quickly into the atmosphere of carbonic acid, it is possible to be so easily stupified, that there is danger of suffocation. In deeper hollows, or in districts where exhalations of carbonic acid are abundant, it is dangerous to enter without having previously let down a lighted lamp.

Carbonated springs are always situated at the lower part of mountain declivities, or at the deepest points of valleys, generally near brooks. Exhalations of gas from fissures in rocks, on the contrary, generally occur at higher points, upon the declivity of mountains. Fresh-water springs issue at points still higher above the bottom of the valley, and sometimes at tolerably considerable heights. All these relations can be observed in the neighbourhood

\* German edition, Vol. 1, p. 258, et seq.

of Burgbrohl, and in the valley towards Gleys. At the former place mineral springs, gaseous exhalations, and a fresh spring, are crowded together within a narrow surface, and are situated in the above-described order. Carbonated springs are always ascending. They can originate only from the contact of ascending water with subterranean exhalation of carbonic acid, at a greater or less depth.

For the purpose of more simple description, we will assume that water absorbs, under all pressures, an equal volume of carbonic acid. Under a pressure of  $n$  atmospheres, it would therefore absorb a quantity which at the ordinary atmospheric pressure would occupy a space equal to the  $n$ -fold volume of the water.\* At a depth of 192 feet, where there is a seven-fold atmospheric pressure, water must, when saturated, contain a quantity of carbonic acid which, at the ordinary pressure, would be equal to seven times its volume. When this water ascends in its channels, the pressure decreases, and at a depth of 160 feet, where there is a pressure of only six atmospheres, a quantity of gas, equivalent to one volume at the ordinary pressure, is disengaged. The water which issues is under the ordinary pressure; therefore it contains a quantity of carbonic acid equal to only its own volume, the other six volumes having been evolved during the ascent. Consequently, under the assumed conditions, the volume of the gas evolved from the spring would be six times as much as that of the water issuing.

At Neusalzwerk the water flows at the rate of a cubic foot in a second, and if the above conditions existed there, 6 cubic feet of carbonic acid would be evolved in the same time. Such an evolution of gas probably never takes place from any channel.

The carbonic acid evolved at this place ascends in innumerable small bubbles; for since the pressure gradually decreases during the ascent of the water, the gas can only escape in very minute bubbles, which do not unite on account of the velocity with which they rise. For this reason the water flowing out appears entirely in the form of a white foam. This phenomenon is similar to the effervescence on opening a bottle of champagne.

\* At the ordinary temperature and pressure, water absorbs 1.06 times its volume of carbonic acid. But Couerbe found that the volume of gas absorbed is not, as was previously supposed, in direct proportion to the pressure, but that it was in a less proportion. Independent of the free carbonic acid in water, there is a portion of this gas which holds the carbonates in solution, and is generally said to be in a state of partial combination. The quantity of this carbonic acid in any one water is, of course, always the same at all depths as at the surface, and it is proportionally greater the more carbonates the water contains. When such mineral waters are exposed to the air, or heated, this portion of the carbonic acid does not escape until after that part which has been merely absorbed.

If carbonic acid escapes from the water which rises in a boring in minute bubbles, it is evident that the quantity of this gas coming in contact with ascending water at unknown depths, cannot amount to more than this water is capable of absorbing under the hydrostatic pressure to which it is there exposed.

The evolution of gas from carbonated springs is different. There is scarcely a mineral spring rich in carbonic acid, from which the gas is evolved only in small bubbles. Among the hundreds of such springs which I have had an opportunity of observing, I have never met with one in which, besides innumerable small bubbles, there were not also larger ones. The former generally ascend in the centre, the latter more at the side of the spring. The large bubbles are not unfrequently observed to rise at regular intervals, so that they may be employed as a measure of time.\*

The difference in the *ascent* of gas from a boring, and from carbonated springs, is owing to the circumstance, that the channels of the latter are never so regular as those of the former. The course of natural springs is, indeed, frequently very irregular; and the more irregular they are, the less does the gas escape in small bubbles.



If we imagine the course of an ascending spring, from the deepest point *a* to its issue *d*, to be represented by the above figure, then while the water rises from *a* to *b* small bubbles would be disengaged, and move along the roof of the channel, *b c*, more slowly, the greater its inclination. During this slow progression,

\* Twenty years ago I visited a mineral spring (Bellerbor, near Coborn, on the Moselle), situated in a very narrow, deep valley, in the clay-slate formation. I observed that the carbonic acid very seldom escaped in separate bubbles; but suddenly a very rapid evolution commenced, which lasted about half a minute. Four months later I was again at this place, and observed precisely the same phenomenon.

however, the small bubbles which continue to be disengaged from the water on account of the decreasing pressure unite, forming larger bubbles, and these upon reaching the perpendicular channel, *c d*, rise rapidly to the surface. During the ascent of the water from *c* to *d*, small bubbles are of course still disengaged, which rise without uniting together. This will represent a spring, from which large bubbles escape at regular intervals, and at the right hand side of the basin *d*, while small bubbles are distributed throughout.

The quantity of gas disengaged in small bubbles depends upon the height of the channel *c d*. If, for instance, it were 32 feet, and the water at *c* saturated with gas, then the volume of the latter would be nearly equal to that of the discharged water. According as the channels are more or less inclined or perpendicular, according as large or small quantities of carbonic acid are absorbed by the water, equivalent modifications in the evolution of the gas will ensue, and it is easy to see how inferences may be drawn as to the configuration of the channel from the character of this evolution.

If a carbonated spring should be found which evolved carbonic acid only in minute bubbles, this would be a sure sign that the water ascended in a more or less perpendicular channel. If, on the contrary, the channels are of a form similar to that represented in the above diagram, and the part *c d* not very high, very few small bubbles can be disengaged during this short passage; therefore large bubbles alone appear, which have been formed in the inclined channel, *b c*, by the union of the smaller ones. If *c* is very near the surface, then only large bubbles can escape. This occurs where a bed, impervious to air and water, covers the surface. It may then happen that *b c* is horizontal, or very nearly so, and a spring ascending to *b*, passes for a long distance under the bed of clay, before reaching the opening *c*, where this bed is broken through. On account of the technical application of the carbonic acid exhalations in the valley of Burgbrohl, I had an opportunity of seeing several mineral springs enclosed. Sometimes I found that the channels of the springs extended for a long distance horizontally.

If the carbonic acid enters the channel at the side, and at a slight depth below its issue, a spring is formed which may present an abundant evolution of gas, and at the same time be poor in fixed constituents. The carbonated water cannot dissolve much, if anything, during the short passage from *c* to *d*.

Mineral waters rich in alkaline carbonates can only be formed



when the water impregnated with carbonic acid remains long in contact with rocks containing alkaline silicates. The formation of such mineral waters, then, can only be imagined as possible when carbonic acid has access to the retentive stratum in which water stagnates. Since even those waters which are richest in carbonate of soda (as the water of the Josephsquelle at Bilin) contain only 0.4%, while a saturated solution contains 20 times as much, it is evident that the carbonated water never remains so long in contact with the rocks as to become saturated with the products of their decomposition. This, indeed, would only be possible when the water in the fissures of the rocks was continually supplied with fresh carbonic acid.

For the formation of a saturated solution of bicarbonate of soda by the decomposition of a silicate of soda, the same quantity of water must gradually absorb at least 23 times its volume of carbonic acid. At a depth of 704 feet, the pressure is equal to 23 atmospheres, and the temperature  $14^{\circ} 6' F.$  above the mean local temperature of the surface. The temperature of thermal waters shows that springs ascend from still greater depths. But notwithstanding the possible conjunction of these conditions for the absorption of such a large quantity of carbonic acid by the water as must be supposed to be present to effect this decomposition, the fact that 0.4% bicarbonate of soda is about the maximum which is found in any mineral waters, shows that this degree of decomposition never takes place.

From the measurements which will subsequently be given of the carbonic acid evolved from springs, and the water simultaneously discharged from them, it follows that the volume of the carbonic acid does not very considerably exceed that of the water. According to all observations that have been made, the inference may fairly be drawn, that such a quantity of carbonic acid as would be necessary for the formation of a saturated solution of bicarbonate of soda, never comes in contact with water.

Upon the earth's surface, the decomposition of crystalline rocks goes on very slowly. In the interior, where they are in constant contact with carbonated water under a greater or less pressure, this decomposition is undoubtedly much more rapid, but still it requires very long spaces of time. Perhaps contact, lasting for an entire year, would be necessary for the saturation of water with bicarbonate of soda originating in this action. However, such a stagnation of water would only be possible if collections of water of enormous extent existed beneath the surface. Such collections

of water do indeed exist; however, it is only in limestone rocks which contain caves of considerable extent, and never in rocks which have but few interstices. In short, the circulation of water—its ascent, and the influx of meteoric water—goes on too rapidly to allow a long stay of the carbonated water between the fissures of the rock which is undergoing decomposition.

Neither could this saturation be effected even if carbonic acid were constantly supplied to the water, as soon as it is consumed in the decomposition of the silicate of soda. In this case, indeed, the increase of bicarbonate in the water might act as a hindrance to the further absorption of gas.

Lastly, it is evident, that in springs, the temperature of whose water but little exceeds the mean local temperature, and consequently comes from slight depths, only still smaller quantities of bicarbonate of soda can be dissolved. In this case there is no considerably elevated pressure to favour the absorption of a larger quantity of carbonic acid; the circulation of the water goes on more rapidly than in thermal springs which ascend from great depths, and the circumstances are therefore much less favourable to solution than in the latter.

Trommsdorff\* was the first to estimate the quantity of carbonic acid given off from exhalations. He found that the gas-spring at Kaiser-Franzenbad yielded 2,102,400 cubic feet of carbonic acid in the year, containing far less than  $1\frac{1}{2}\%$  of sulphuretted hydrogen.

I have found that a gas-spring near Burghöhl yields 1,546,505 to 2,062,250 cubic feet, or 196,370 to 261,705 pounds, of carbonic acid annually; and that the gas issuing from the boring at Neusalzwerk amounts, annually, to 1,576,800 cubic feet, at  $91^{\circ}$  F., and 28  $7\frac{1}{4}''$  barometer, containing 93.86% carbonic acid.† The volume of water flowing from the boring is 20 times as great as that of the gas issuing. The carbonic acid retained in absorption by the water, amounts to 0.722 of its volume. The discharged brine, therefore, carries off 22,768,992 cubic feet annually. Consequently, the carbonic acid evolved as gas, and that carried away by the water, amount together to 24,248,976 cubic feet in the year.

The quantity of carbonic acid evolved, is to that remaining absorbed in water (the acid which the carbonate dissolves included)

\* Die Mineralquellen zu Kaiser Franzenbad bei Eger. Osann und Trommsdorff, 2te Aufl. 1828, p. 134.

† The method of accurately determining the quantity has been described in the German edition. Vol. 1, p. 275.

as 1 : 15·36. Now, since the pressure equal to one atmosphere, or a column of water 32 feet high, retains the latter portion of the gas, there is, besides this, the pressure of a column of water equal  $\frac{32}{15 \cdot 36} = 2\cdot08$  feet, necessary to hold in absorption the carbonic acid evolved as gas. At the small depth of about 2 feet under the water level in the boring, then, the evolution of carbonic acid from the brine commences. Below this point it is in complete absorption.

When this boring was made, the evolution of carbonic acid did not commence until a depth of 1580 feet was attained. Here fissured rocks were reached, and the flow of water increased considerably. It is at this depth at least, then, that the carbonic acid first comes in contact with the water, and here they are exposed to a pressure equal to  $50\frac{3}{5}$  atmospheres. Since the carbonic acid enters the water under such a pressure, its volume, compared with that of the water by which it is absorbed, is very small: it cannot be more than about one-fiftieth that of the latter.

Even the water flowing from this boring, and evolving such considerable quantities of carbonic acid, does not contain the quantity of gas which would be necessary for the formation of a carbonated spring, whose water would contain the quantity of bicarbonate of soda present in that of the Josephsquelle, at Bilin, even if it came in contact with silicates containing soda, during its subterraneous course.

I have already had occasion to make measurements of the relative quantities of carbonic acid and water which mineralsprings yield.\* I found the quantity of gas issuing from a spring in the neighbourhood of Burgbrohl, which may perhaps be considered as one of the richest in carbonic acid, to be 4,237 cubic feet in 24 hours, the water flowing in the same time being 1157 cubic feet. As the water contains 1·65 times its volume of free and half-combined carbonic acid, the total quantity of this gas amounts to 6,146 cubic feet in 24 hours, and is therefore 5·3 times that of the water. The temperature of the water issuing from this spring, exceeds the mean local temperature by about 9° F.; it would, therefore, come from a depth where there is a hydrostatic pressure equal to  $14\frac{3}{5}$  atmospheres. Admitting that, at this depth, carbonic acid has access to the water in such quantities as completely to saturate it, there would be three times as much absorbed.

Another mineral spring near this, from which, likewise, a very considerable quantity of gas is exhaled, and where the relative

\* Poggendorff's Ann. Vol. 32, p. 250.

quantities of gas and water could be measured with greater accuracy, yields, in 24 hours, 3,063 cubic feet of carbonic acid, and 3,645 cubic feet of water. Since the water contains 1.55 times its volume of free and half-combined carbonic acid gas, the total quantity is here 8,713 cubic feet in 24 hours, consequently 2.4 times the volume of the water. The temperature of the water in this spring is about 9° F. above the mean temperature of the neighbouring fresh springs, and therefore, comes from a depth where there is a hydrostatic pressure equal to about  $14\frac{3}{8}$  atmospheres. If, at this depth, carbonic acid came in contact with the water in such quantities as to saturate it, there would be nearly 6 times as much absorbed.

It can scarcely be doubted, that at least the greater part of the carbonic acid comes into contact with the water of the above springs at the deepest parts of their watercourses. But in this case, the large bubbles rising in them cannot be unabsorbed gas, but gas which was in absorption at greater depths, and has been disengaged from the ascending water, in consequence of the lessened hydrostatic pressure. The circumstance of the gas issuing chiefly in large bubbles, indicates, as was previously shown (p. 225), that the spring-channels are irregular.

If there are instances in which carbonic acid passes unabsorbed through the water of springs, it is when the temperature of these waters but little exceeds the mean local temperature that this is most probable. In such springs the water comes into contact with the exhalations of carbonic acid at a comparatively short distance below the surface, where, consequently, the hydrostatic pressure determining the absorption of the gas is small. If, at the same time, much gas is exhaled from such springs, it may be conjectured that the carbonic acid passes unabsorbed through the water, and especially so when the quantity of water discharged is small.

Bunsen\* found the quantity of carbonic acid annually exhaled from the artificial brine-spring at Nauheim (p. 221), to be 8,859,200 c. ft., at 91° F., *i.e.* 1,000,000 pounds. Two other springs at the same place yield about 4,000,000 cubic feet. He found, from the comparison of the quantities of gas and water discharged, that the latter was sufficient to absorb the entire quantity of the free carbonic acid, under a pressure of 2 or  $2\frac{1}{2}$  atmospheres, besides that gas contained in the water. The boring is 114 feet deep, and the pressure at the bottom is, consequently, equal to 4 atmospheres. It may, therefore, be

\* Studien des Göttingischen Vereins bergmännischer Freunde. Vol. 4, p. 3 61.



assumed with great probability, that at the lower part of the boring the gas is in perfect absorption, and is not evolved until the water rises. The disengagement of the gas is itself the source of a considerable power for the raising of the water; for when the opening of the boring was contracted to 3 inches diameter, the column of water ascended through a tube 10 feet in length, and then rose about 8 feet in the air. When the boring was closed and opened again after a few minutes, the water rose in the above-mentioned beautiful column (p. 221). The analysis of gas collected at a depth of 3 feet in the boring, did not afford a trace of foreign admixtures.

One of the exhalations at Marienbad, which a few years since was enclosed for gas-baths, and furnished with conducting tubes, yielded annually, according to Heidler,\* 1,314,000 c. ft.; the bath-spring at Pyrmont, according to V. Graefe,† at least 1,226,400 c. ft.; and all the channels there together, at least 6,570,000 c. ft. According to Suadiciani,‡ the mineral spring at Driburg yields 2,190,000 c. ft. of carbonic acid. These quantities are exceeded by those of both springs at Meinberg, which annually yield, according to Piterit,§ 10,512,000 c. ft.

Neusalzwerk, Pyrmont, Driburg, and Meinberg, are situated in the midst of sedimentary strata, far distant from volcanic districts or basaltic rocks. Fr. Hoffmann|| mentions, besides, a considerable tract of land upon the left bank of the Weser, where carbonic acid is exhaled, wherever the variegated sandstone underlying the muschelkalk is exposed. It cannot, therefore, be doubted that by boring deep enough, in any part of this tract, carbonic acid would be found. The strong evolution of carbonic acid from the boring at Neusalzwerk is, therefore, not to be regarded as an isolated phenomenon.

All the mineral springs (the boring of Neusalzwerk excepted) of this tract, more or less rich in carbonic acid, have a low temperature, little exceeding the mean local temperature. Their water, therefore, comes in contact with carbonic acid at a slight depth, and the pressure to which this gas is exposed cannot amount to more than a few atmospheres.

All these exhalations, besides those of Neusalzwerk, of carbonic acid originate in the variegated sandstone. Their seat cannot,

\* Pflanzen und Gebirgsarten Marienbads, p. 170.

† Die Gasquellen, &c. 1842, p. 403.

‡ Hufeland's Journ. Vol. 14, p. 11.

§ Über die Gasquellen Meinberg's, p. 20.

|| Poggend. Annal. Vol. 17, p. 156.

therefore, be sought in any younger formation. At Meinberg, indeed, they issue from fissures in muschelkalk and keuper; but as it is in the highest degree probable that all the exhalations in this district have a common source, those at Meinberg would likewise originate in the variegated sandstone.

It has been attempted to ascribe to exhalations of carbonic acid a share in the elevation and rending of strata.\* But these exhalations are without doubt so universal, and branch out in such various directions in the interior of the earth, that if the gas meets with obstacles at one point, it will issue at another, although perhaps far distant. The immense quantity of gas which now escapes from the borings at Neusaltzwerk and Nauheim, indisputably existed beneath the strata before they were pierced; but it had previously other means of exit, and it issues here only because this boring offers fewer obstacles.

If the Rhenish transition formation were to sink beneath the sea, and a new sedimentary period were to commence, all the exhalations in the environs of the Lake of Laach, &c., would cease, because they would not be able to overcome the pressure of the water, but they would seek other passages where there were fewer obstacles.

The exhalation of carbonic acid from unknown, but certainly very great depths, admits of the inference that they must be free from atmospheric air. If, however, traces are found, they originate in water which has conveyed it in absorption to the spring-channels. According to the known law, that water containing one gas evolves a corresponding quantity upon absorbing another, the water coming in contact with streams of carbonic acid and absorbing it, would give up the atmospheric air which it had absorbed at the surface. This air would mix with the carbonic acid rising from the springs. Its quantity is, however, so small that it can rarely be estimated. This proves that the air which water conveys below the surface is insignificant compared with the

\* Fr. Hoffmann, p. 153. He refers to Stiff's observation, according to which the numerous springs of Nassau, so rich in carbonic acid, almost always issue from spots where the adjoining exposed strata have suffered remarkable alterations in the dip and strike, and saddle-shaped elevations occur. These are described as being phenomena similar to those which occur in Westphalia, and are considered to be evidence in favour of continuous subterranean agency. It would be superfluous to controvert such inferences. Rending of the strata, saddle-like elevations of sedimentary beds, so thick as the transition formation, cannot possibly have been caused by exhalations of carbonic acid, which have comparatively so small a pressure. This gas issues wherever channels penetrate to the focus of its evolution, but it cannot have formed these channels by rending the strata.

quantities of carbonic acid encountered. This is so much the more the case in proportion as the volume of carbonic acid evolved from a spring is relatively greater than that of the water discharged. Those springs, then, which are most abundant in gas, and poorest in water, yield gas which is freest from atmospheric air, and the reverse.

All the carbonic acid exhalations of the Lake of Laach—and I have examined very many—are of tolerably equal purity. Caustic potash absorbed the gas, with the exception of a small bubble. I found the gas from the Meinberg and Driburg mineral springs to be equally pure, as well as that from the marshy plain near Istrup.

The exhalations of the Laach district are quite free from sulphuretted hydrogen; for if they contained a trace of this gas, it would be perceptible in the factory at Burgbrohl, where the carbonic acid is employed for the precipitation of white lead. There is no doubt that when carbonic acid is accompanied by sulphuretted hydrogen, the latter has its origin much nearer the surface than the former, and comes from sedimentary strata which contain sulphates and organic remains.

According to Brandes,\* the exhalations from the Meinberg springs, as well as those of Pyrmont and from the so-called Dunsthöhle, with the exception of the medicinal bath and brine-springs, contain no sulphuretted hydrogen.

The following investigations show that the gases evolved from the Rhenish mineral springs contain more nitrogen and oxygen the greater their distance from the Laach district.†

GASES EVOLVED.

	From the Fellenbor near Burgbrohl.	From the mineral spring at Heppingen.	From a mineral spring at Ehlingen in the Ahr Valley.	From the mineral spring at Roisdorf.	From the Godesberg mineral spring.	
					First experiment.	Second experiment.
Carbonic acid ... ..	99.116	98.189	96.303	93.685	81.120	81.506
Nitrogen ... ..	0.708	1.408	3.372	6.061	18.545	17.717
Oxygen ... ..	0.176	0.403	0.325	0.254	0.335	0.777
The percentage of the two latter gases was :	100.000	100.000	100.000	100.000	100.000	100.000
Nitrogen ... ..	80.115	77.778	90.88	95.973	98.225	95.800
Oxygen ... ..	19.885	22.222	9.12	4.027	1.775	4.200

\* Die Mineralquellen zu Meinberg, p. 303.

† My investigations (German edition, Vol. 1, p. 307 and 308) shew that the gases absorbed by mineral waters have not the same composition as those which are evolved from them.

As the proportion of oxygen in the exhalations from the latter three springs is much smaller than in atmospheric air, a part must have been consumed in oxidation, probably of proto-carbonate of iron.

The great purity of the carbonic acid from Fehlenbor, a mineral spring situated in the midst of very considerable gaseous exhalations, shows that in this case the quantity of atmospheric air carried below the surface by meteoric water, is insignificant compared with the quantity of carbonic acid exhaled. While at Roisdorf, Godesberg, &c., where these exhalations are mere local phenomena, the quantity of atmospheric constituents in the gases exhaled is considerably greater. At Neusalzwerk the same relations present themselves. Here is only one exhalation, and 6 per cent. of atmospheric air is mixed with the carbonic acid. This spring is remarkably rich in water, and this accounts for the quantity of atmospheric air.

In districts where the fissures for a considerable distance around are all filled with carbonic acid, it is easy to perceive that the exhalations must contain less atmospheric air; because the water penetrating into the earth, will lose the greater part of its atmospheric air by displacement before reaching the point where the formation of mineral water takes place; while at other places where the exhalations are merely local, the descending water, which does not come in contact with carbonic acid before reaching this point, retains its atmospheric air.

If the circumstance that the proportion of oxygen in relation to nitrogen in many gaseous exhalations is smaller than in atmospheric air, results from the partial combination of this gas with oxidizable substances, it might be expected that the gases evolved from warm springs would contain still less oxygen than those which issue from cold springs, for the higher the temperature of the water the greater would be the oxidation. This is really the case, as the following analyses show.

L. Gmelin and Lade found that the gas issuing from the Kochbrunnen, at Wiesbaden, consisted of 82·3% carbonic acid, and 17·7% nitrogen.\* Monheim found the gas from the Kaiserquelle, at Aix-la-Chapelle, to contain only nitrogen, carbonic acid, and 0·5% sulphuretted hydrogen. I found it to contain 7% oxygen. He also found in the Pockenbrunnchen, at Burtscheid, only nitrogen, carbonic acid, and 0·1% sulphuretted hydrogen. But I found 2% oxygen in this gas. The gas from the Burtscheid

\* Poggendorff's Annalen. Vol. 7, p. 467.



medicinal spring, Monheim found to have very nearly the same composition as that from the Pockenbrünnchen. He also found in the gas from the Kochbrunnen, the hottest of the Burtscheid springs, besides nitrogen and carbonic acid,  $0.1\frac{0}{0}$  to  $0.15\frac{0}{0}$  oxygen.\* According to my analysis, the gas of the Kochbrunnen consists of—

Carbonic acid	...	...	47.3
Nitrogen	...	...	52.1
Oxygen	...	...	0.6
			<hr/>
			100.0

this being the mean of three closely corresponding analyses. Finally, according to Anglada, the gas evolved from the sulphuretted springs of the Pyrenees is pure nitrogen.†

The carbonic acid evolved either from collections of water or from fissures, is distinguished from the artificial by a peculiarly pure taste and smell. As the permanent exhalations of carbonic acid originate without exception from deeper springs (p. 218),‡ the gas would be freed from any impurities by the water.

Twenty-six years ago I showed the processes by which it is possible that carbonic acid exhalations may originate, and proved that even if atmospheric air could penetrate to the seat of their formation, the carbonic acid would always be accompanied by nitrogen. Even if all the oxygen were converted into carbonic acid, still the gas exhaled must contain 79% nitrogen. But there is no carbonic acid exhalation which contains this quantity of nitrogen.

In the sedimentary strata, where a former organic world is buried, we find the material for the formation of carbonic acid by decay. If such a process took place there, it might be expected that we should find the most abundant exhalations of carbonic acid where the greatest masses of coal are buried. Those exhalations only, which issue from strata more recent than the coal formation, can reasonably be considered to originate from coal. But these exhalations are by no means the most considerable, and are, on the contrary, insignificant compared with those which issue from the transition rocks inferior to the coal-formation, as is

\* Die Heilquellen von Aachen, Burtscheid, &c. 1829, pp. 209, 232, et seq. Poggendorff's Annalen, Vol. 32, p. 244.

† Mémoires pour servir à l'histoire générale des eaux minérales sulfureuses et des eaux thermales, 1828; and Ann. de Chim. et Phys. Vol. 20, p. 246.

‡ Vulkanische Mineralquellen. 1826, p. 255, et seq.

shown by the frequently mentioned exhalations of the Laach district, the Eifel, Taunus, &c.

The absence of carbonated springs in those districts where the coal-formation is at the surface, proves that the vegetable remains buried in sedimentary strata are not the source of the carbonic acid exhalations. While in the transition rocks of the Eifel these springs are so numerous, there is not a single one in the coal districts of Saarbrücken and Aix-la-Chapelle.

On the other hand, very different gaseous exhalations issue from the coal-formation, undoubtedly originating from coal or from the strata filled with organic remains, and alternating with the coal-beds; these exhalations consist of the combustible pit-gas, mixed with a small per-centage of carbonic acid gas. However, we shall see in Chapter XV that, under certain circumstances, pure carbonic acid gas may also be evolved during the decay of organic substances. Moreover, with regard to quantity and importance, the exhalations of combustible pit-gas are not to be compared with those of carbonic acid in districts where carbonated springs are abundant.

In no case can carbonic acid exhalations originate from brown coal in the way which Liebig is inclined to assume.\*

At every part of the earth where observations have been made, the temperature increases with the depth below the surface. If this same increase goes on at depths which are inaccessible, there must be a red heat at a certain depth. If at this depth there are beds of carbonate of lime, carbonic acid would be disengaged from them in the same way as in limekilns.

According to geognostic observations, the transition rocks of the Rhine have a thickness of at least four miles. If the temperature continues to increase at the same rate that it does within accessible depths, there must be at the lower boundary of these strata a temperature of 463° F. Carbonic acid is not disengaged from carbonate of lime at this temperature. If, therefore, this rock exists under the transition formation, it must be situated very deep under it.

Since carbonic acid exhalations frequently appear after volcanic eruptions, continuing long as moufettes after violent eruptions of Vesuvius,† and since we recognise these exhalations in districts

\* *Die Organische Chemie, &c.*, 1841, p. 300. See Bischof, German Edition, Vol. 1, p. 313, for my remarks upon this view.

† Monticelli and Covelli. German translation, 1824, pp. 191—196. The carbonic acid exhalations, after eruptions of Vesuvius, are very considerable. On

which were undoubtedly the former seats of volcanic action, as in the Auvergne Vivarais, the Eifel, Lake of Laach, &c., it appears probable that in these cases they are the last effort of volcanic action. Where, as at these places, melted masses (lava) have at a former period risen to the surface, it is possible that there was a red heat at a much less depth, by which the carbonic acid would be disengaged from carbonate of lime.\*

But when we see that carbonic acid issues from deep borings, as at Neusalzwerk and Nauheim, in districts where there is not the least trace of former volcanic action, it is necessary to be cautious in ascribing these exhalations in all cases to this source.

Carbonate of lime, magnesia, and protoxide of iron, are decomposed by silica and boiling water (Chapter I, No. 3); when they, therefore, occur together with quartz in the interior of the earth, and are exposed to the action of hot water, they will be decomposed and carbonic acid will be expelled.

The boiling springs show that a temperature of at least  $212^{\circ}$  exists where they originate. Admitting that the depth at which the temperature rises  $1^{\circ}$  F. is 51 feet, and that this increase advances in an arithmetical series, it would follow that at a depth of 8,000 feet in our country there is a temperature of  $212^{\circ}$  F.† There can be no doubt that the transition-formation extends below this depth. But at many places the increase of temperature towards the centre is much more rapid. Thus Graf von Mandelsloß‡ found in a boring at Neuffen, on the north-west foot of the

the 15th of June, 1794, they killed more than 1300 hares, and numbers of pheasants and partridges in the preserves. They even exercise their destructive influence upon the fish in the sea. Hamilton states, that some fishermen of Rosina observed, near some rocks of old lava which projected into the sea, and from under which carbonic acid escaped, a large swarm of fish, swimming about at the surface, in great inquietude. Ebelmon (*Comptes rendus*, Vol. 20, No. 19) is of opinion that this carbonic acid proceeds from the decomposition of carbonates by silicious minerals, at a high temperature. But if this were the case, we might expect that the gas would be evolved during volcanic eruptions. However, Monticelli and Covelli did not find it in the smoke of Vesuvius, but only in that which issued from the lava, and then not until its temperature had sunk below  $212^{\circ}$  F.

If we see that, by boring, channels can be opened in sedimentary formations, through which carbonic acid rises, so likewise, by the ascent of lava in these rocks below Vesuvius, channels may be opened, through which the same gas may rise. In this case, then, the carbonic acid would not be produced by volcanic action, but only caused to escape from the interior of the earth.

\* *Vulkanische Mineralquellen*, &c., p. 251, et seq.

† *Physical, Chemical, and Geological Researches on the Internal Heat of the Globe*, by G. Bischof. London, 1841, Vol. 1, p. 193.

‡ *Neues Jahrbuch für Mineralogie*, &c. 1844, p. 440.

Swabian Alps, an increase of temperature amounting to  $1^{\circ}$  F. at a depth of 17 feet. At a depth of 1,140 feet, there was the extraordinary temperature of  $102^{\circ}$  F. If the increase goes on in the same proportion, there would be a temperature of  $212^{\circ}$  F. at a depth of 2,800 feet. This boring, from a depth of 697 feet to its lowest point, passes through lias-limestone; and if this rock extends to a depth of 2,800 feet, and at that depth contains quartz, it is very possible to conceive the disengagement of carbonic acid under the above-mentioned conditions. A temperature of  $212^{\circ}$  F. has already been reached at a depth of 45 to 60 feet near the Lago di Monte Rotondo. According to Payen, the gas of the Suffioni of Tuscany contains  $57\cdot3\%$  carbonic acid. According to Fr. Hoffmann,\* the aqueous vapours of the lagunes at Monte Cerboli issue from fissures in limestone. Near the great Fumachie di Castelnovo, fine granular sandstone with a marly cement preponderates. Here are all the conditions necessary for the disengagement of carbonic acid: carbonate of lime, quartz, aqueous vapour, and a temperature of  $212^{\circ}$  F. at a moderate depth. It is, therefore, in a high degree probable that the carbonic acid in the Suffioni is disengaged in the way above mentioned.

It is then no longer necessary to assume that there are beds of limestone at great depths, where there is a red heat, in order to account for the stupendous phenomenon of carbonic acid exhalations: the necessary conditions are found at far less depths.

The question whether carbonic acid may exist in a liquid form at great depths and under high pressure, cannot be satisfactorily decided in the present state of science.†

Evolutions of gases from fissures and rents, are mentioned in several accounts of earthquakes,‡ and may, perhaps, be the cause of the destruction of fish in lakes and in the sea during earthquakes, several instances of which are known. The restlessness and howling of animals, both wild and tame, which are reckoned among the indications of an approaching earthquake, and which there is an inclination to ascribe to mephitic gases, which they recognise by their keener organs of sensation and their greater proximity to the surface of the earth, might equally be connected with a sudden disengagement of carbonic acid.§

\* Poggendorff's Annal. Vol. 26, p. 61.

† German edition, Vol. 1, p. 332, et seq.

‡ Humboldt's Reise in die Äquinoctial Gegenden. Vol. 1, p. 499; V. Hoff. in Poggendorff's Annal. Vol. 7, p. 292; Vol. 9, p. 593, and Vol. 25, p. 76.

§ It is, however, to be inferred that the mephitic gases evolved during many earthquakes are not merely carbonic acid, but contain likewise sulphuretted



The question, where our well-waters obtain the quantity of carbonic acid necessary for the solution of lime, magnesia, &c., is not so easily decided.

Twenty-six years since, I took considerable pains to direct attention to this subject.\* The meteoric water which penetrates into the earth, contains atmospheric carbonic acid. The gas is also generated in the vegetable mould by decay, and is absorbed by the water.

The water of all rivers contains carbonate of lime and magnesia (p. 80) in solution, and we find them in the water of wells which they feed, always in greater quantity than in river water. Thus, the well of the laboratory at Bonn contains 3 times as much carbonate of lime as the water of the Rhine near Bonn. The quantity of free carbonic acid in this water is, however, scarcely sufficient to dissolve this excess of carbonate of lime. The well is 58 feet deep; therefore, the Rhine water moves far below the vegetable mould; and as under this is an impervious bed of loam, no carbonic acid can be conveyed from thence to this water. Upon the left bank of the Rhine, near Bonn, the brown-coal formation lies upon the sides of the valleys, and it is probable that it extends underneath the diluvium of the Rhine. The carbonic acid generated by the decay of its organic remains, may perhaps penetrate through the sand and gravel, and is absorbed by the water in the depth. It is not unfrequent for a stratum of carbonic acid, several feet in height, to collect above the water of deep wells, and workmen have frequently been suffocated in consequence. It cannot be supposed that this carbonic acid is evolved from the well-water, which is far from being saturated with carbonic acid. It might indeed be expected that this gas, upon entering the well, would be completely absorbed by the water.

The quantity of carbonate of lime which is annually extracted by the Pader, Lippe, &c., from the Teutoburger Wald, is equal to a cube of more than 100 feet. For the solution of such a cube of limestone, 779 million pounds of carbonic acid would be necessary.

It is not probable that the carbonic acid which the meteoric waters abstract from the atmosphere can be sufficient for this solution.

The evolution of carbonic acid in mines, in the neighbourhood

hydrogen, from the circumstance that, in the accounts of earthquakes, mention is sometimes made of a smell of sulphur vapours. Humboldt, loc. cit. p. 484, et seq.; Hoff. loc. cit., Vol. 12, p. 567; Vol. 18, p. 46.

\* Vulkanische Mineralquellen, p. 270, et seq.

of which carbonated springs are not present, shows that the formation of this gas by decomposition of organic remains, really does go on in the interior of the earth.

When the gases evolved from springs contain nitrogen in greater proportion than atmospheric air, the deficient oxygen has been consumed in the oxidation of organic substances (p. 234). The experiments of Rich. Phillips, jun.,\* have confirmed this; for on conducting a gentle stream of air over 200 grains of soil, he obtained 6 grains carbonic acid. The same will happen when meteoric water, charged with oxygen, comes in contact with organic matter in rocks. The greatest quantity of oxygen which water can retain, would, when entirely converted into carbonic acid by organic matter, yield as much as would enable the water to dissolve  $\frac{1}{3570}$  its weight of carbonate of lime. This quantity, indeed, corresponds tolerably with the carbonate of lime in the above-mentioned rivers of the Teutoburger Wald, and there is no want of organic matter in the chalk where these rivers rise. But the gas which is evolved from them, as well as that held in solution, always contains more or less oxygen (p. 208); therefore, only a part of that originally present has been converted into carbonic acid. If, finally, it is recollected that meteoric water never contains the maximum quantity of oxygen, it remains very doubtful whether the carbonic acid which this water brings with it from the atmosphere, and that which is formed by the oxidation of the organic remains in the chalk at the cost of its oxygen, amount to so much as to be able to dissolve that large quantity of carbonate of lime.

If, as we have previously seen, large quantities of carbonic acid are evolved from variegated sandstone, this may also be the case where this formation is covered by younger strata. It is, therefore, not to be doubted that the waters of these rivers may possibly obtain carbonic acid also from the interior of the earth.

Since exhalations of carbonic acid are, as has been proved by the above remarks, by no means merely local, but tolerably universal phenomena, it is possible that the water of rivers which penetrate laterally through beds of sand and gravel, not unfrequently acquire carbonic acid from subterranean sources.

From the fact that carbonate of lime decomposed a solution of a per-salt of iron with evolution of carbonic acid, Stein† has attempted to show that this process is a hitherto disregarded source of carbonic acid in nature. He supposes the per-salt of iron to be

\* Phil. Mag. Vol. 26, No. 174.

† N. Jahrbuch für Mineral., &c. 1845, p. 801.

derived from decomposing pyrites. It cannot, indeed, be doubted that in many cases carbonic acid originates from this source. The conversion of carbonate of lime into gypsum, is not an unfrequent phenomenon near iron pyrites. On washing, the latter are frequently found to contain traces of sulphate of lime. But whether this process can be regarded as going on upon a scale sufficiently large to account for exhalations of carbonic acid like those of Pyrmont, as Stein supposes, appears to me doubtful. Moreover, iron pyrites very rarely occurs in limestone.

## CHAPTER XIII.

### CARBON.

By far the greater part of the carbon existing upon or in the earth is contained in the sedimentary formations; it occurs in the most concentrated form in the various kinds of coal. That these are the remains of past vegetation, is proved by the still recognisable forms of plants and vegetable organs found in them. The carbonaceous masses in minerals have likewise the same origin.

#### A.—*Graphite.*

This substance occurs chiefly in gneiss, mica schist, and clay-slate, in beds which are not unfrequently very regular; disseminated in nests forming veins, in granite and porphyry, and in deposits of magnetic iron-ore. In the gneiss at Passau, it occupies the place of mica.\*

If the above-mentioned crystalline rocks were of igneous origin, and the graphite was present in the fused mass, the same results would have followed which are observed in our iron furnaces: the proto- and persilicates of iron would have been deoxidized; and even if the reduced iron was subsequently oxidized, in consequence of the penetration of water, hydrated oxide of iron must still have been found in them, together with proto-silicate of iron.

If gneiss, mica slate, &c., were rocks which had been metamorphosed by igneous agency, then the silicates of iron would likewise have been reduced during the metamorphic change; for

\* There is in the Edinburgh Museum a fine specimen of this kind.

these substances are reduced by carburetted hydrogen and carbonic oxide at moderate temperatures; and these combustible gases would have been evolved by the organic remains in the sedimentary rocks under the influence of igneous agency. On melting powdered basalt with as much graphite as was necessary to reduce its oxide of iron, I found that the cooled mass contained brilliant particles of metallic iron, and when powdered and boiled with dilute sulphuric acid, gave off hydrogen. On igniting the powdered mass with oxide of copper, a small quantity of carbonic acid was evolved. There was, consequently, still some graphite remaining. If, therefore, graphite was formed simultaneously with the other constituents of crystalline rocks, these rocks could not have assumed their present condition in consequence of igneous agency. But if it has been introduced subsequently, there must have been an equivalent displacement of other minerals.

Graphite also occurs very frequently in granular limestone, and not unfrequently together with minerals which contain silicates of iron, such as hornblende, augite, &c. If granular limestone had been formed from sedimentary limestone by the metamorphic agency of heat, the graphite would have decomposed not only those silicates, but also the carbonate of lime, carbonic oxide being formed and the base set free. There would, therefore, have been no traces of graphite left. If a granular limestone containing disseminated graphite be ignited, the evolution of carbonic acid and carbonic oxide may be recognised.

Among the minerals imbedded in the granular limestone of Auerbach, in the Bergstrasse, is magnetic pyrites, whence arises the evolution of sulphuretted hydrogen when it is treated with hydrochloric acid. If this carbonate of lime be washed with hot water, scarcely perceptible traces of sulphate of lime are found; but if, on the contrary, it be ignited previous to being washed, such a quantity of this salt is found that chloride of barium gives an abundant precipitate. This shows decisively that the granular limestone in question cannot have been exposed to the influence of a high temperature. I shall subsequently show that granular limestone can only have been formed by aqueous agency. This is, therefore, the only conceivable mode in which the graphite and accompanying minerals can possibly have been formed.

Even the purest graphite contains traces of earthy matter. One of the purest varieties from Wunsiedel contained, according to Fuchs,\* 0.33%. Dumas and Stass,† as well as Erdmann and

\* Journ. für pract. Chemie. Vol. 7, p. 353.

† Annal. de Chim. et de Phys. Vol. 3, Sér. 1, p. 5.



Marchand,\* obtained by the combustion of graphite, previously carefully purified, a residue of silica. In the impure varieties, the quantity of iron, lime, and alumina amounts to as much as 37%. Karsten† and Sefström have proved that the iron in graphite is only an admixture. The presence of earthy matter in graphite admits of the inference that it is of organic origin.

The formation of graphite during the smelting of iron has been brought forward as an argument in favour of its igneous origin. It separates in this process partly in the form of fine scales in the interior of the cast iron, and in cavities in the slags, as well as in large crystals in the stones of the furnace. It has been asserted that graphite occurs only in the upper parts of the slags, and it has been inferred from this that it has been deposited from the gaseous form, not only here, but also where it occurs in fissures and clefts, and even in sedimentary rocks.‡ We must not, however, forget that the fact of carbon being one of the least volatile substances known, is greatly opposed to this assumption. The transfer of carbon, observed in the discharge of a powerful galvanic battery between charcoal-points, and its deposition in the form of graphite upon the negative pole, has indeed been frequently brought forward as a counter-argument. Fizeau and Foucault§ regard this formation of graphite, under the influence of a high temperature, as having an important bearing upon the study of those minerals in which this variety of carbon is so frequently met with; and Haidinger|| appears even inclined to explain, by such a process, the formation of the pseudomorphous graphite in forms of iron-pyrites in a meteoric stone. But how is it in the remotest degree possible to ascribe the formation of graphite in the fissures of clay-slate, or even in meteoric stones, to a galvanic discharge? Haidinger himself does not doubt that this rare pseudomorph was formed when the meteoric stone, after reaching the earth, was exposed to the influence of our atmosphere, and, consequently, was long ago cooled. It would be very difficult to conceive the formation and discharge of a voltaic circuit in this stone. It is, moreover, altogether erroneous to attempt to explain the causes of geological facts by the aid of supposed analogies with the action of the complex apparatus of physical cabinets, whose existence in nature could

\* Journ. für pract. Chemie. Vol. 23, p. 159.

† His Archiv. Vol. 12, p. 91.

‡ Cotta Jahrbuch für Mineral. &c. 1834, p. 39; and Bronn, Handb. einer Geschichte der Natur. Vol. 2, p. 625.

§ Poggend. Annal. Vol. 63, p. 475.

|| Ibid., Vol. 67, p. 437.

scarcely be conceived by the boldest and most unrestrained imagination.

The separation of graphite from cast iron belongs to a class of phenomena which are frequently observed in the solidification of heterogenous melted masses. It takes place from a cast iron highly overcharged with carbon, after the cooling and solidification; for if the quantity of carbon is greater than the cast iron is capable of retaining after solidification, the excess must separate. It must separate from slags the more readily, as it does not enter into combination with the oxides of which they consist. The separation of graphite in crystals, would appear to admit of the conjecture that the carbon existed in a liquid state in these melted masses. But it is undoubted, that it is in this state only when combined with iron; and it is possible, that fluid iron contains more carbon than solid iron, and that consequently, upon cooling, a part separates. It is also conceivable that coal strongly heated and slowly cooling, may crystallise without being previously melted.\*

It cannot appear strange that the formation of graphite in the reduction of iron and in the preparation of coal-gas, when drops of empyrematic oil continually fall back into the retorts at the same spot, forming grey stalactitic masses of metallic lustre, should have led to the view that it was of igneous origin. Since, however, all natural relations point out the possibility of its formation by aqueous agency, the circumstance that we are unable to form it in this way cannot afford any grounds for scepticism. We are likewise unable to form coals from organic substances, and yet it could scarcely be doubted by any one that such was their origin. Every circumstance indicates that the formation of coal was a process which went on with extreme slowness, under circumstances which we are unable to imitate. If, therefore, neither these condi-

\* I have a slag from an iron furnace, in which the matrix is of a whitish, somewhat grey colour, studded with extremely bright and thin laminae of graphite, partly of considerable size, partly in minute points. Small drusy cavities are likewise coated with such laminae. Here and there larger unaltered fragments of coal, seldom containing particles of graphite, are imbedded in the mass. The conditions necessary for the conversion of this charcoal into graphite, do not appear, therefore, to have existed, or not to have continued long enough. The whitish colour of the slag shows the absence of proto-silicates of iron, and the presence of particles of iron in it, show that the protoxide of iron has been reduced by the great excess of carbon. Another green iron slag contains many hollows, generally lined with lamina of graphite, near which granules of iron are always imbedded. Here the reduction of the proto-silicate of iron is very evident; this graphite is undoubtedly the remainder of the carbon not consumed in that process.

tions nor the enormous periods of time concerned in the formation of coal are at our disposal, and if, as is highly probable, graphite is a product of the still further advanced alteration of organic matter, we cannot possibly expect to produce this substance by the process followed in nature, although we may do so by the influence of heat in a short period. Ligneous substances are known to be capable of carbonization both by the influence of heat and of water. In the former case, the change proceeds rapidly; in the latter, with extreme slowness, as is shown in the case of piles under water. But the final products are in both cases essentially the same, the only exception being, that when resulting from the more gradual aqueous agency, it is very coherent; when resulting from igneous agency, light and porous. In both cases the carbonization is completed when the gaseous constituents—hydrogen, oxygen, and nitrogen—are mostly removed, and graphite is nothing more than carbon freed from these substances.

Only one pseudomorph consisting of graphite is known. Partsch and Haidinger\* found graphite in the form of iron pyrites in the meteoric mass of Arva.†

It follows from what has been remarked, that all the localities of graphite afford evidence in favour of its being a product of the alteration of organic matter by aqueous, and not by igneous agency. This is very distinctly shown by the coal-beds of Karsok, in the Omenaks-Fiord, in the Danish colonies of North Greenland, according to the observations of H. Rink, of Copenhagen.‡ Graphite is said to occur in beds in the coal-formation near Cumnoch, Ayrshire.

### B.—*Anthracite.*

This substance is undoubtedly to be classed among the remains of altered organic matter. In its nature it resembles coal, although its formation, as is indicated by its geological situation, is frequently much more ancient, and therefore the organic character is still less recognisable than in coal. Anthracite occupies an intermediate position between coal and graphite. However, the fibrous

\* Poggend. Annal., Vol. 67, p. 437.

† The substance of the pseudomorph affords an incontrovertible proof that it can only have been produced by aqueous agency. As, however, the still obscure formation of meteoric stones is a subject beyond the limits of this work, I must refer to the German edition, Vol. 2, p. 70.

‡ I have seen specimens of the graphite found here, at Dr. Krantz's, who possesses several. The discoverer has not, however, stated whether it occurs in coal or tertiary coal.

anthracite is of contemporary formation with coal, and forms thin beds in it.

According to the analyses of several kinds of anthracite by Regnault, L. Gmelin, Woskressensky, Jacquelin, W. R. Johnson, Voelcker, &c., it contains—

Carbon	....	75.00	....	95.00
Hydrogen	....	1.49	...	3.92
Oxygen }	....	0.29	....	3.45
Nitrogen }				
Water	....	1.59		
Ash ....	....	0.94	....	7.07

The presence of volatile substances, the association of vegetable impressions and organic remains\* with anthracite, and its occurrence in sedimentary formations,† wholly exclude the possibility of ascribing its formation to the influence of a high temperature.

### C.—*Diamond.*

If it was desired to adopt the hypothesis that simple substances existed in an isolated state previous to the existence of compounds, and that these had in the course of time originated from the combination of simple bodies, then the diamond might fairly be regarded as a primitive substance; for even gold, and still less platinum, do not occur in such a high state of purity as this precious stone.

So long as the diamond was only known to occur in alluvial deposits, in rivers and rocky detritus, almost every hypothesis as to its origin was admissible; for it is found associated with the most different kinds of rock. In Hindostan, it is found in

\* Thus, the anthracites of Isère and Tarentaise consist of altered formations with coal plants and lias shells. Those from Schönfeld, near Freyberg in Saxony, occur in irregular alternation with beds of feldspathic porphyry, conglomerates, sandstones and carbonaceous schists, passing into each other in a very varied manner.

† In clay-slate and grauwacke, anthracite forms nests and whole beds, sometimes of considerable thickness. It likewise occurs in beds, between mica-schist and alum-schist, and in dykes in alum and grauwacke slates, with calespar, in trap rocks, as well as in veins of quartz and silver ore, &c. If all these localities afford decided evidence in favour of its formation by aqueous agency, it cannot be incorrect to attribute to the same origin the anthracite occurring upon the surfaces of fissures in granite. The minerals accompanying anthracite are depositions from water, and by the gradual decomposition of organic substances, which are never wanting in water, anthracite is formed.



a sandstone breccia, consisting of granules of hornstone quartz, chalcedony, jasper, cornelian and brown iron-ore, forming a bed for the most part only a few feet in thickness, at a greater or less depth below the surface, and not unfrequently covered by thick strata of sandstone. In Borneo, diamonds occur, according to Horner,\* in a thick bed of red clay, beneath which are quartz gravel or fragments of syenite or diorite, and less frequently beds of marl, with existing species of marine shells (*ostræa cordium*). They are accompanied by magnetic iron-ore, scales of gold and platinum, as well as granules of iridium and osmium. The first diamond found in the Ural, was taken from an auriferous sand, between crystals of iron pyrites and fragments of quartz. Some of those more recently found had black spots, probably owing to the presence of coal. It appears that the original locality of these diamonds was a black dolomite.† In the province Constantine, in Africa, diamonds are found in the auriferous sand of the river Gumel. In Brazil they are found associated with small laminæ of native gold, and generally in rounded grains and crystals in ferruginous sand and clay. They are accompanied by transported fragments and rounded crystals of quartz, specular and micaceous specular iron, brown iron-ore, jasper, chalcedony, disthene, chrysoberyl, anatase, native gold and platinum; likewise fragments of clay-slate and talcose-slate occur.

It is evident that all these minerals cannot have been derived from the same rock. All detrital deposits, especially in valleys, must naturally contain fragments of all the rocks of the entire stream region. Moreover, the circumstance that, in Brazil, the quartz pebbles are united together by a cement of brown iron-ore, in which diamonds are situated, can in no way speak in favour of their common origin; for this cementation may have been effected by ferruginous water. The association of diamonds with gold and platinum, is probably for the most part merely accidental, since, according to recent observations, diorite sometimes contains these metals, although no diamonds have been found in this crystalline rock.

There is in the Museum at Rio de Janeiro a tolerably large rounded diamond with very distinct impressions of quartz grains; the latter, therefore, existed previously to the crystallization of the carbon.

It was not until a few years since that the native rock of

\* Poggendorff's Annal., Vol 60, p. 526.

† G. Rose, Reise nach dem Ural, Vol. 1, p. 352, et seq.

diamond was fortunately discovered in Brazil. According to Helmreichen, Claussen, and Lomonosoff,\* it is the itacolumite. The diamonds are of various sizes, with rounded but brilliant surfaces, and firmly imbedded in the quartz of the native rock. Some geologists consider itacolumite to be a rock metamorphosed by igneous agency. There cannot be a more erroneous opinion than this, for it is impossible that a rock containing the hydrated minerals, chlorite and talc, should have sustained the action of heat. The itacolumite which, according to Eschwege, forms a system of strata in Brazil, in some parts more than 100 miles in length, is a sedimentary rock. If, as is not to be doubted, metamorphic processes have taken place in it resulting in the production of mica, talc, and chlorite, they can only have been effected by aqueous agency. Therefore, the diamonds occurring in this rock can likewise only be products of similar metamorphism, for which organic remains have afforded the material.

Sir David Brewster read a communication to the Royal Society of Edinburgh, in 1820, on the occurrence in some diamonds of a polarizing structure, occasioned by the existence within them of small portions of air, "the expansive force of which has communicated a polarizing structure to the parts in immediate contact with the air." According to Dumas and Stass,† the diamond leaves a yellowish residue on combustion in oxygen gas, amounting to  $\frac{1}{2000}$  or  $\frac{1}{5000}$  of its weight. Erdmann and Marchand‡ likewise obtained about  $\frac{1}{10000}$  of a reddish ash. These experiments were, however, always made with unpolished diamonds, which were not quite colourless. Petzholdt§ states that, by microscopic examination, he has observed a similarity to the vegetable cell-structure in these residues, which he also found in the interior of a dark-brown diamond. Silica and iron were detected in the ash by means of the blowpipe. Wöhler|| could not recognise any indications of vegetable structure in 50 diamonds which he examined, all containing inclosed substances. Nothing respecting the origin of the diamond can, therefore, be deduced from these experiments.

\* Comptes rendus, 1843. No. 1, p. 38, and No. 3, p. 87. Poggendorff's Annal., Vol. 58, p. 474. Compare also Eschwege, Claussen, and Denis, in the Jahrb. für Mineral, &c., 1842, pp. 459 and 605. Lucas detected, in the year 1815, two diamonds in a piece of itacolumite (Nouveau dictionnaire d'Hist. Nat., Art. Diamant). In 1827, a negro slave found the first imbedded diamond; and in 1836 the diamond mines were worked in the itacolumite of the Serra de Grao-Mogór.

† Annal. de Chimie et de Physique, 3 Sér., Vol. 1, p. 5.

‡ Journ. für pract. Chem., Vol. 23, p. 159.

§ Beiträge zur Naturgeschichte des Diamants. Dresden and Leipzig, 1842.

|| Annal. der Chemie u. Pharm., Vol. 41, p. 346.

Several chemists have unsuccessfully attempted to crystallize carbon by igneous agency.\*

Liebig† considers the formation of diamonds as the final result of a process of decay. He says, "If we suppose decay to proceed in a liquid rich in carbon and hydrogen, then, as in the production of naphthaline, there will be formed a substance gradually becoming richer in carbon, from which carbon itself would at last be separated, and in a crystalline form, as the final result of its decay. Besides the process of decay, science affords no analogies which will account for the origin of the diamond. It is known with certainty that its formation is not owing to the action of heat, for a high temperature and the presence of oxygen are incompatible with its combustibility. On the contrary, there are satisfactory grounds for believing that diamonds have been formed in the humid way, that is, in a liquid, &c." Jameson long ago suggested that the diamond was of vegetable origin. G. Wilson‡ considers anthracite is probably one of the substances most likely to crystallize into the diamond. In a chemical point of view, these hypotheses do not admit of any objection. Now, since the occurrence of the diamond speaks only in favour of a formation by aqueous agency, every hypothesis as to its igneous origin must be rejected as totally unfounded. Moreover, diamonds could not have been formed by igneous agency in rocks containing silicates of iron, for the carbon would have been consumed in the reduction of the iron, as is proved by the following experiments. A diamond

\* "The late Kenneth Kemp endeavoured to crystallize carbon from its vapour, by producing the voltaic arc between charcoal points within the Torricellian vacuum. It may, perhaps, be questioned whether carbon was truly vapourized in this experiment, or only detached in the state of minute particles from the intensely heated charcoal; at all events it did not crystallize, but was deposited as an impalpable soot on the sides of the barometer-tube." Wilson. (Ed. New Phil., Jour. April, 1850.) Silliman made similar experiments many years ago, and witnessed, as he believed, the true fusion and volatilization of carbon, but did not obtain it in distinct or transparent crystals (Amer. Jour. of Science and Arts, Nov. 1849, p. 413). Jacquelin has shown that the diamond, when suddenly exposed to the intense heating power of voltaic electricity, changes into coke or graphite (Comptes rendus, Vol. 24, June, 1847). The formation of the diamond by igneous agency would, therefore, pre-suppose that carbon crystallizes at a temperature which is lower than that produced by voltaic electricity, while at a higher temperature the crystalline carbon is again rendered amorphous. But this would be a very singular assumption. Despretz has exposed charcoal to the combined influence of a powerful voltaic current, the concentrated rays of the sun, and the blowpipe. Small needles of anthracite, exposed to this triple source of intense heat, seemed to fuse, and drops fell from them, which, when received on a platinum capsule, appeared as minute black globules. These globules may have been only the ash of the anthracite coloured by charcoal. (Comptes rendus, June 18, 1849, p. 755.)

† Die organische Chemie, &c., p. 473.

‡ Loc. cit.

weighing 0.25 grain was mixed with pure peroxide of iron and exposed to a strong heat. Its edges and corners were rounded, it assumed a milk-white colour like opal, and lost 0.06 grain of its weight. The residual oxide was attracted by the magnet, showing the presence of iron. When powdered augite, which had previously been strongly ignited, was mixed with powdered diamond, and heated to bright redness in a porcelain retort, carbonic acid gas was evolved. Part of the oxide of iron in the silicate of the augite was therefore reduced.

If aqueous processes take place in such a rock as itacolumite, producing new minerals, it is not improbable that by a concurrence of decomposition processes in mineral and organic substances, a gradual separation of hydrogen, nitrogen, and oxygen from the latter may be effected, so that finally carbon alone remains, and in a crystalline form. The rare occurrence of the diamond shows that it is not every kind of decomposition of organic substances which will yield it, for were it the final result of every kind of decay, it would be more abundant.

The evolution of carburetted hydrogen and carbonic acid in coal mines, shows that the separation of hydrogen and oxygen is a process which is still going on in coal-beds, as well as in the decaying plants of bogs. The identity of the products of decomposition resulting from a process which is just commencing, with those resulting from one which has undoubtedly been in progress for millions of years, enables us to recognise the increasing tendency of nature to separate and isolate carbon from its associates in dead organized bodies, and the flames of burning coal show that this isolation has not nearly been accomplished.

If, then, nature has not succeeded in accomplishing this isolation by a process which has been going on almost from the first appearance of the vegetable kingdom on the earth,—if by decay of such long duration diamonds have not been formed,—it cannot but appear remarkable that this substance should be found in rocks which are of far more recent formation than those of the coal series. In a still more ancient formation—clay slate, the oldest of the sedimentary rocks in which vegetable remains have been found—there is an anthracite coal still containing hydrogen and oxygen; and although the graphite, likewise present in this rock, is free from these substances, still it has not been rendered crystalline.

It is, therefore, evident that diamond is not formed by decay alone, whether going on in large masses, as in the coal-beds, or in



the fissures of rocks. Special conditions must be present. The frequent occurrence of graphite in mica slate, a rock which closely resembles itacolumite, appears moreover to suggest that the processes by which graphite and diamond are formed are not very dissimilar.

Peroxide of iron is reduced to protoxide when in contact with decaying organic matter, and the presence of organic matter is an important condition in the formation of iron pyrites. Here are inorganic and organic substances in a state of reciprocal action. Perhaps both reactions consist in the separation from the organic matter of a hydrocarbon, which converts the peroxide of iron into protoxide, and the sulphates into sulphurets, thus removing the hydrogen while the oxygen is evolved from the organic substance as carbonic acid. These are not imaginary processes, but actual ones; and as we see, that where organic substances are decomposed without the presence of inorganic substances, the hydrogen and oxygen are evolved in combination with carbon, the analogy is in favour of the assumption that in contact with inorganic substances the hydrogen and oxygen are evolved from the mixture in the same compounds. In short, we can without difficulty imagine, that by the reduction of peroxide of iron and sulphates at the cost of organic matter, the hydrogen and oxygen of the latter would gradually be completely separated, and that the isolated carbon would be capable of crystallising *in statu nascenti*.

The association of diamonds with brown iron-ore, which in the Ural has originated in the decomposition of iron pyrites, is in perfect accordance with this view. It is also worthy of notice, that in the province of Minas Geraes, in Brazil, the diamonds occur in conglomerate, firmly cemented by hydrated peroxide of iron, presenting much similarity to our bog iron-ore, and certainly of very recent formation. This similarity with a mineral which has demonstrably been formed by the reciprocal action of peroxide of iron and decaying organic substances, greatly favours the above view.

#### D.—*Origin of Carbon generally.*

The geologists who ascribe to the earth an igneous origin, can adopt no other view than that all the carbon upon and in the earth is of secondary origin, and therefore was not present at the period of creation; for the reducing agent of the iron-ores would not have remained in contact with peroxide of iron and other oxides in the state of igneous fusion without being converted into carbonic acid

and carbonic oxide gases, thus causing the reduction of the oxides. Since the entire group of unstratified crystalline rocks, which, according to the hypothesis of the plutonists, have been ejected from beneath, contain in their masses no carbon, this fact must lead them to the conviction that this substance cannot possibly be an original formation.

The foregoing considerations show that even carbon in its purest form, as the diamond, can only be regarded as a product of the decomposition of organic substances. So long, therefore, as carbon in the unoxidised state, and bearing all the marks of not having resulted from decomposed organic substances, is not shown to be present in rocks, we cannot regard this simple body as one which existed at the time of creation. Carbon, like all the other simple bodies, occurs very sparingly, or not at all, in the mineral kingdom; just as we find all the other simple bodies, with the exception of chlorine, bromine, iodine, and fluorine, chiefly in combination with oxygen, and such of them as form the chief constituents of rocks only thus combined; so we find carbon also, *as a constituent of rocks*, only in the oxidized condition in carbonates; we thus find it, also, in the exhalations, in waters and in the atmosphere.

All the carbon yet known to occur in the isolated condition can therefore only be regarded as a product of decomposition of carbonic acid, and it is the vegetable kingdom which yielded and still yields this product.\*

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## CHAPTER XIV.

### EXHALATIONS OF CARBURETTED HYDROGEN.

ON the western shores of the Caspian, in the country round Baku, upon the peninsula of Abscheron, a tract has been long known under the name of the *Field of Fire*, which continually emits inflammable gas, while springs of naphtha and petroleum occur in the same vicinity. By an extensive series of observations upon the temperature of springs and wells,† Abich found the medium temperature of the soil of Abscheron to be 59° F., that of the

\* German edition, Vol. 2, p. 95, et seq.

† Zeitschrift der deutschen geologischen Gesellschaft. Vol. 3, p. 45.

naphtha  $62\cdot5^{\circ}$  to  $66^{\circ}$ , and that of the gas-springs  $68\cdot5^{\circ}$ : the gas, therefore, can only come from moderate depths. Upon the Schagdag, not far from the village of Kinalughi, 7,834 feet above the Caspian sea, are found considerable exhalations of carburetted hydrogen gas (the *Eternal Fire* of the Schlagdag) which stream directly out of clefts in sandstone alternating with slate. This burning gas is never extinguished by meteorological influences.

Among the numerous other places where carburetted hydrogen is evolved, we mention only the following: Pietramala, in the Tuscan Appenines; from a brook at Bedlag, below Glasgow\* (known now for upwards of 40 years); at Klein-Saros, in Transylvania,† &c. Such exhalations are of very frequent occurrence in coal-pits, where they proceed partly from fissures in the adjacent rock (blowers), partly from the coal itself. It cannot be definitively shown that inflammable gases are evolved from brown coal; from bituminous layers of clay iron-stone, however, this may well take place. Carburetted hydrogen gas is also frequently evolved from springs: thus, from the Adelheid spring, near Benediktbeuern;‡ from the hot springs at Aix-la-Chapelle ( $0\cdot26$  to  $1\cdot82\%$  of the volume of all gases which were exhaled or evolved from the water when boiled);§ from the sulphuretted springs at Nenndorf ( $0\cdot17$  to  $1\cdot46\%$ );|| the springs at Niederlangenau, in the country of Glatz ( $8\cdot02\%$ );¶ the Herkulesbad, in the environs of Orsova, in Banat ( $0\cdot38$  to  $0\cdot88\%$ ).\*\* Such small quantities of carburetted hydrogen may yet be detected in many exhalations of gas. During the sinking of bores, large quantities of them are met with very frequently.

Exhalations of carburetted hydrogen are of frequent occurrence in rock-salt formations. The first notices of this fact were communicated by Guettard,†† and Marcel de Serres.‡‡ Bremer§§ gave intimation of an inflammable gas which, since the 18th of March, 1826, has been constantly streaming forth at a depth of 45 fathoms from a fissure in the clay-marl deposited in the rock-salt in the mine of Ludovici, at Szlatina, in Hungary, and is employed to light the mine. Such an exhalation had been observed there pre-

\* Bald in Edinb. Journ. of Science. July, 1829, p. 67.

† Gilbert's Annal. der Physik. Vol. 37, p. 1, et seq.

‡ Schafhäult, im Jahrbuch für Mineralogie. 1846, p. 688.

§ Bunsen, Poggendorff's Annal. Vol. 83, p. 252.

|| Ibid., p. 253.

¶ Poleck, im Journ. für pract. Chemie. Vol. 52, p. 353.

\*\* Ragsky, in Jahrbuch der oestreichischen geologischen Reichsanstalt. 1851, Vol. 2, p. 93.

†† Mém. sur la mine de sel de Wieliczka, Mém. de l'Acad. 1762, p. 512.

‡‡ Essai sur les manufactures de l'empire d'Autriche. Vol. 2, p. 374.

§§ Poggendorff's Annal., Vol. 7, p. 131.

viously.\* From an old pit, which has not been wrought for 86 years, in the salt-work of Gottesgabe, at Rheine, in the county of Tecklenburg, an inflammable gas is evolved, which, after 1824, was employed during several years to supply light and heat. About one cubic foot of gas was exhaled every five minutes. According to Eaton,† carburetted hydrogen is evolved in three places on the south side of the Erie channel, in the State of New York, from a bed of rock-salt, under which lies an extensive coal-bed 600 feet thick. At Rocky Hill, on the Ohio, a mile and a half from Lake Erie, while boring for rock-salt, an exhalation of combustible gas was met with, which continued in large quantity for a considerable time.‡ About two miles to the south of this lake an inflammable gas issues from a boring in Stinkstein, in such quantity as to be employed to light the village of Fredonia. The light of the flame of this gas is not so lively, however, as that of the artificial gas§ In the district of Marietta, in the State of Ohio, the inflammable gas is a constant attendant upon brine-springs; so that its appearance, while boring in search of rock-salt, is looked upon as an indication of a successful result.|| In the country round Tseu-lieou-tsing, in China, exhalations of inflammable gas from brine-wells are, according to the communications of the missionary Imbert, very common.¶ Some of these are employed merely for the sake of the inflammable gas, which is yielded in so large a quantity that it is used to boil the brine, as also to heat and light the buildings in which the salt is prepared. The brine in one of these wells having ceased, the bore was continued to the depth of 3,000 feet; the brine did not again appear, but when the borer had reached this enormous depth, a stream of gas suddenly made its appearance, which was employed as fuel. There are wells, the gas of which, when lighted, yields a flame 30 feet in height; here the gas seems to come from beds of coal, for it has often been met with in bores.

I. Dumas,\*\* found that the gas which is evolved from the so-called crepitating rock-salt of Wieliczka, on being dissolved in water, is inflammable. H. Rose†† examined this gas, and found that it appeared to be a mixture of carburetted hydrogen and hydrogen.

\* Geographisch-Historisches und Producten-Lexicon von Ungarn, 1786, p. 713.

† Silliman's Journ., Vol. 15, p. 237.

‡ Edinb. Journ. Vol. 10, p. 186.

§ Journ. of the Royal Institution, Vol. 1, p. 203.

|| Silliman's Journ., Vol. 10, p. 5.

¶ Bibliothèque Universelle, Vol. 40, p. 318, and Comptes rendus, Vol. 22, p. 667.

\*\* Annal. de Chim. et Phys., Vol. 43, p. 316.

†† Poggendorff's Annal, Vol. 48, p. 353. In the galleries of the rock-salt



According to Bunsen,\* this gas consists of—

Carburetted hydrogen gas	....	....	84.60
Oxygen gas ....	....	....	2.58
Carbônic acid gas	....	....	2.00
Nitrogen gas	....	....	10.35
			<hr/>
			99.53

The inflammable gas in the crepitating salt must be present in a state of strong compression, for Dumas and H. Rose found that the salt yields half its volume of gas. Different pieces of salt yielded, however, unequal quantities of gas. Under the microscope no cavities can be detected in it; while being dissolved in water its lamellæ become thinner, inside these there form small bubbles of gas, which separate the lamellæ from one another (by which the cracking is effected), and escape by the fissures so produced. The clear and transparent pieces of the crepitating salt decrepitate on being dissolved, just as the cloudy and non-transparent specimens.

The crepitating salt does not appear to be peculiar to the rock-salt mines of Wieliczka; at Hallstadt, in Austria, such a crepitating salt also occurs. (Chapter XVIII.)

#### ANALYSES OF COMBUSTIBLE GAS FROM COAL-PITS.

	BISCHOF.†			TH. GRAHAM.‡	
	I.	II.	III.	IV.	V.
Carburetted hydrogen gas	83.08	91.36	79.10	94.2	82.5
Olefiant gas....	1.98	6.32	16.11	.....	.....
Oxygen gas ...	.....	.....	.....	1.3	1.0
Nitrogen gas ...	14.94	2.32	4.79	4.5	16.5
	100.00	100.00	100.00	100.0	100.0

mine of Wieliczka, the inflammable pit-gas not unfrequently collects in the roofs. Its presence is often revealed by the crackling sound which it produces. Hrdina, in Karsten's and Von Dechen's *Archiv. für Mineralogie*, etc., Vol. 16, p. 797. May not the evolution of the gas from the crepitating salt in these cases, perhaps, depend upon the latter coming in contact with water?

\* Loc. cit., p. 251.

† Edinb. New Phil. Journ., Vol. 29, p. 309, and Vol. 30, p. 127.

‡ Phil. Mag. and Journ. of Science, 3rd series, No. 189, p. 437. More than

I. A blower from a fissure in sandstone in the coal-formation of Gerhard's Stollen, in Louisenthal, near Saarbrücken.

II. A blower from a fissure in slate-clay at the bottom of the gallery of a coal-mine near Wellesweiler, about 20 miles from Saarbrücken.

III. Inflammable gas evolved from an artesian well in a pit in the principality of Schaumburg.

IV. Inflammable gas from the coal-mines of Gateshead, near Newcastle.

V. Inflammable gas from the coal-mines of Killingworth (?), near Newcastle.

The gas I flows out with no higher pressure than that of atmospheric air. The gas II, however, flows out with a pressure greater than that of the atmospheric air; for it was evolved from the floor of the mine, which was covered by water to the depth of several inches. Both gases were tasteless and without odour. The gas III is evolved with force. These three gases troubled lime-water. I and II contain 4% of carbonic acid gas. They contain no determinable quantity of oxygen, and no vapoury hydrocarbons which are condensible by sulphuric acid. The gases I and II have a temperature which is only about 3° to 6° F. higher than the medium temperature in the places where they occur. They can, therefore, only proceed from depths of 112 to 155 feet below the galleries.

The gas V suffered a diminution of volume when treated with chlorine gas in the dark; since, however, phosphorus became strongly luminous in it after a little air was added, while an admixture of  $\frac{1}{400}$ , or even less, of olefiant gas removes this luminosity, Graham concluded that the gas last mentioned was absent.

In No. I, chlorine gas gave rise to so trifling a diminution of volume, that the existence of olefiant gas remains somewhat doubtful; should it be present, it cannot, according to this loss, exceed 0.25%. Chlorine gas indicates, No. II, from 2.8 to 3.8%, and in No. III 6.56% of olefiant gas. According to Graham's experiments, therefore, it appears doubtful whether these three gases actually contain olefiant gas. Whence comes it, however,

30 years ago, analyses of combustible pit-gases were made by Henry, Thomson, II. Davy, &c. Since that time, however, advances have been made in this analysis. In general, the results which those chemists have obtained agree with the above. The presence of olefiant gas, however, is not indicated in any of their analyses.

that chlorine absorbs quantities so very unequal, although the experiments were instituted under exactly the same circumstances? The quantities of oxygen, also, which these three gases required for detonation, and from which their composition was estimated, stand nearly in the same relation as the amounts of chlorine absorbed. Lastly, the gas No. III was somewhat more easily ignited than No. II, and the flame of the former was more luminous than that of the others, which also point to the presence of olefiant gas. I have not made the experiment with phosphorus.

No. IV and V contained no carbonic acid gas. Might it not perhaps have been already absorbed by the water?

No. I, II, IV, and V. were evolved from the oldest coal-formation. The gases which were previously analyzed by Henry, Thomson, and Davy, were also, so far as I know, from similar sources. But the gas No. III was from a much newer coal-formation, viz., one belonging to the lias series.

The chief constituent of all these pit-gases, therefore, is carburetted hydrogen, sometimes mixed with small quantities of olefiant gas and carbonic acid gas. Nitrogen seems to be invariably present; it cannot be derived from atmospheric air in those instances in which it issues with force from fissures, but is no doubt a product of the decomposition of organic substances, most probably of the coal itself. The similarity of the pit-gases to marsh-gas, is much in favour of the view that such is the origin of the nitrogen.

Carbonic oxide was not to be found in any of these five gases. Bunsen,\* likewise, could not detect the smallest traces of this gas in various exhalations containing carburetted hydrogen. Seeing, indeed, that the exhalations of carburetted hydrogen undoubtedly proceed from the decomposition of organic substances in the wet way (Chapter XV), and that under these circumstances carbonic oxide is never developed, this gas was hardly to be expected in such exhalations. The low temperatures above given of the exhalations of Abscheron, where volcanic action in the depths might be conjectured, exclude the notion that heat has any share in their formation. Bunsen could not even find any combustible constituent containing carbon in many fumaroles examined upon Iceland, though they are undoubtedly in connection with volcanic agency. Wherever exhalations of carburetted hydrogen occur volcanic action cannot exist.

\* Loc. cit., pp. 241 and 253.

## CHAPTER XV.

## COAL—BROWN-COAL—ASPHALT—AMBER—AND OTHER PRODUCTS OF DECOMPOSITION OF VEGETABLE MATTER.

“COAL may be expected to occur, under favourable circumstances, in all sedimentary formations; but there is only one which is everywhere so rich in beds of coal that it has received the name of the ‘coal formation.’ This formation consists of the strata lying immediately above the transition rocks.”\*

The occurrence of vegetable remains in all kinds of coal is such convincing evidence of its formation from vegetable substances that all further proof is superfluous. If the immense quantities of coal present in the old coal formations be compared with the small quantities which have been deposited in the subsequent secondary rocks, the latter appear quite insignificant. On the other hand, if it be considered that, after the elevation of the younger formations from the sea, the extent of the continents has continually increased, and consequently vegetation also, the question arises, where are the remains of successive vegetations to be sought? Since the remains of plants, grown previously to the old coal formation, are found in it, there is no sufficient ground for the assumption that those which have grown in later periods should have wholly perished. There are two circumstances which might throw a light upon the disappearances of the plants of this period: firstly, the presence of large quantities of bituminous substances in many secondary rocks; and, secondly, the appearance and great increase of gigantic animals, the remains of which are found in these formations.

Various rocks, slates, and limestones contain frequently very large quantities of bituminous matter, amounting to 10% and more. Their thickness is, not unfrequently, so great that we might imagine the formation of considerable masses of coal if this matter were separated from the rocks, converted into coal, and deposited as seams. The bituminous matter present in many lime-

\* Naumann, *Lehrbuch der Geognosie*. Vol. 2, p. 313.



stones, resulting from the decay of animals or plants (p. 171 and 189), forms a large aggregate quantity. Now, since the quantities of limestones continually increase from the old coal formation to the chalk, inclusive, such of the plants as contributed to the deposition of carbonate of lime could not, of course, go to the formation of coal.

Gigantic animals must have consumed immense quantities of plants; for whether they were herbivorous or carnivorous, their food would, in either case, be derived from the vegetable kingdom.\* Their nitrogenous excrements were not capable of being converted into coal, but into bituminous matter, which also occurs in rocks in which their remains are found.

In tertiary rocks there also occur large quantities of coal, but limestones are mostly wanting here; consequently, the consumption of plants for the deposition of carbonate of lime by organic agency was insignificant in this period. Since those plants only which grow in water are capable of separating large quantities of this carbonate, the land plants, which have chiefly contributed to the formation of brown-coal, cannot have furnished any large quantity of material for the formation of bituminous limestones. It is only the stems of trees petrified by carbonate of lime that have diminished the material for the formation of brown-coal, for by far the greatest part of their organic matter must have been removed in aqueous solution. The remains of large mammiferous animals, entombed in tertiary rocks, show that no inconsiderable quantities of vegetable matter were thus abstracted from the formation of coal in this period.

\* The coprolites (Buckland, in the *Transact. of the Geolog. Soc. of London*, 2nd Series, Vol. 3, p. 223) found in carboniferous sandstone, lias, oolite, Hastings-sand, greensand, chalk marl, and chalk, in the rocks of Maastricht, London clay, in fresh water formations at Aix, and in caves containing bones; their occurrence in lias of Bath, Easton, and of Broadway Hill, at Evesham, in a layer extending to many miles, consisting of them, and amounting to the fourth part of the entire mass, show the geological importance of these excrements of former animals. The coprolites examined by Wollaston consisted chiefly of phosphate and carbonate of lime, and a very small quantity of phosphate of ammonia and magnesia, without organic matter. Prout found, on the other hand, a large quantity of it in fossil sepia from the lias, and, besides phosphate and carbonate of lime, a considerable amount of silica in coprolites from greensand. There can be no doubt that the organic remains were replaced by this silica, and also that the iron pyrites occurring in coprolites owes its formation to them. Coprolites being the excrements of animals eating bones, and consequently consisting for the most part of inorganic matter, they have been preserved until the present time, while the excrements of herbivorous animals have undergone decay, and have therefore contributed to the formation of bituminous matter. If the excrements of gigantic animals of former periods, containing only small proportions of inorganic matter, could have been petrified or converted into coal, considerable quantities of such masses would certainly have been found in secondary formations.

The coal consists chiefly of the stems of *Stigmara*, *Sigillaria*, *Lepidodendra*, and *Calamites*, on the more or less perfectly preserved bark of which may be recognised the characteristic leaf cicatrices, generally by the naked eye. The fibrous anthracite which accompanies all the true coal of the older formations, in beds of from  $\frac{1}{4}$  to  $\frac{1}{2}$  an inch in thickness, shows under the microscope, the well-preserved structure of the *Araucaria*. Besides these, *Calamites* occur in the state of fibrous anthracite, but the other stems very rarely. A considerable share in the formation of coal has erroneously been ascribed to the ferns.\*

There cannot be a doubt that the conversion of vegetable substances into coal has been effected by the agency of water. The different varieties of true coal are for the most part unacted upon by any solvents. Ether and sulphuret of carbon sometimes extract a resinous substance. They all contain water, the compact less than the earthy varieties. They lose this water, according to Regnault, in a vacuum, and at a temperature a little above  $212^{\circ}$ . The presence of nitrogen in coal is shown by the ammonia which it yields on dry distillation, or when heated with potash. It also contains sulphur, independently of iron pyrites. The tertiary coal generally contains much more water than the bituminous coal, and, like this, sulphur, independently of iron pyrites. According to Marx, some tertiary coal is almost entirely dissolved by alkalies. P. Kremer† states that lignite and coal differ chemically, inasmuch as the former yields, by dry distillation, acetic acid and acetate of ammonia, the latter, on the contrary, an ammoniacal liquid. Since it is the woody fibre which chiefly gives rise to the acetic acid obtained by the dry distillation of wood, this would appear to prove that brown-coal contains still undecomposed woody fibre, and that bituminous coal does not contain any, were it not for the fact that humus also yields acetic acid.

There are a great number of analyses of coal and lignite. I have below arranged the results of the greater part of these

\* Göppert, in Poggend. Annal., Vol. 86, p. 482. There are but few varieties of coal in which their vegetable origin can be detected by anatomical examination. Göppert, to whom we are indebted for many valuable researches on coal, and Link, have, however, recognised here and there organic structure, not only in tertiary coal, but even in older coals. Lyell and Witham even detected remains of *Coniferæ* in bituminous coal. In some varieties of tertiary coal (bituminous wood, lignite, &c.), the woody structure is so perfectly preserved, that even the species of the tree may be determined. Generally, however, even in tertiary coal, the change is so far advanced that scarcely anything more can be recognised than a few elementary organs.—Unger Geschichte der Pflanzenwelt, 1852, p. 82.

† Poggend. Annal. Vol. 84, p. 77.

analyses, limiting myself to the statement of the maximum and minimum of constituents, and the average composition. The percentage quantities of organic elements are given after deducting the earthy substances. H. Taylor\* directs attention to a circumstance which certainly has a great influence upon the accuracy of these results; namely, that the earthy constituents of coal retain some combined water which cannot be estimated, on account of the presence of organic matter. When the coal has been dried, as usual, at  $212^{\circ}$ , the chemically combined water and that formed during the analysis are evolved together, consequently the oxygen and hydrogen are estimated too high. This error is greater the more earthy constituents the coal contains, and this circumstance must therefore be taken into consideration in examining the composition from the direct results of analysis.

I. Analyses of nine specimens of coal from the old coal formations of Upper Silesia, Saarbrücken, Essen and Werden, Eschweiler and England; by Karsten:†

Carbon.			Hydrogen.			Oxygen and Nitrogen.			Earthy substances.	
Max.	Min.		Max.	Min.		Max.	Min.		Max.	Min.
96.6	74.8		5.5	0.4		21.1	3.0		2.9	0.5

II. Analyses of eight specimens from the old coal formations of Newcastle, Glasgow, Lancashire, Edinburgh, and South Hetton; by Th. Richardson:‡

89.2	79.1		7.2	5.3		14.5	5.5		14.6	1.1
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III. Analyses of sixteen specimens from the old coal formations of Alais, Rive-de-Gier, Flenuof, Mons, Lavaysse, Epinac, Commentry, Blanzly, Newcastle, and Lancashire; by Regnault:§

90.6	83.0		5.9	4.9		11.8	4.4		5.3	0.24
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IV. Analyses of six specimens from the lias formation in Schaumburg-Lippe, from the lower strata of the lower oolite of Céral (Dép. de l'Aveyron), from the sandstone strata of the greensand of Saint Girons and Gagat from a similar bed to the former, at St. Colombe; by Regnault:

90.4	76.0		5.8	4.9		18.3	4.7		19.2	0.9
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\* Edinb. New Phil. Journ. Vol. 50, p. 140.

† Untersuchungen ueber die kohligen Substanzen des Mineralreiches. 1826.

‡ Annal. der Pharmacie. Vol. 23, p. 42.

§ Annales des Mines, troisième série, Vol. 12, 4 livraison de 1837, p. 161.

V. Analyses of six specimens from the old coal-formation of the Plauenschen Grund, near Dresden ; by Köttig :\*

Carbon.		Hydrogen.		Oxygen and Nitrogen.		Earthy substances.	
Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
81.8	79.1	6.2	5.7	15.1	12.2	27.0	7.5

VI. Analyses of three specimens from the old coal-formation beds of Newcastle (Hartley) ; by H. Taylor :†

87.9	81.0	6.5	5.8	12.8	4.5	16.9	1.4
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VII. Analyses of four specimens from the coal of Newcastle, (Wigan cannell), St. Helen's, Staffordshire, and Oregon ; by F. Vaux :‡

83.1	79.4	6.0	5.3	14.9	10.2	35.5	1.0
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VIII. Analyses of twelve specimens from the old coal-formation in Silesia ; by Baer :§

84.7	74.2	5.6	4.8	20.3	13.3	10.1	2.7
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IX. Analyses of nine specimens from the old coal-formation in Westphalia ; by Baer :

90.4	81.3	5.3	4.5	13.0	5.0	14.1	3.2
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X. Analysis of English coal ; by Baer :

79.0	5.8	15.7
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XI. Analyses of two specimens from the Marennnes of Tuscany (Monte Massi) ; by Bunsen :||

77.2	76.0	5.5	5.1	18.5	17.7	4.1	3.2
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XII. Analyses of two specimens of Russian coal from Krassnokut, near Bachmut, and from the banks of the Oka (Gov. Vladimir) ; by Woskressensky.¶ According to Murchison, &c., they belong to the old coal-formation :

73.1	64.5	5.1	4.7	30.8	21.7	6.5	2.4
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XIII. Analyses of five specimens of Russian coal from Solikamsk, Charkow, Tschernolessnaja, in the Caucasus ; Selenina

\* Journ. für prakt. Chemie. Vol. 34, p. 463.

† Loc. cit.

‡ Quarterly Journal of the Chem. Soc. of London, Vol. 1, No. 3, p. 318.  
These coals contain from 0.4 to 2.6 per cent. sulphur.

§ Archiv. der Pharmacie. 2nd Series. Vol. 61, p. 3, and Vol. 63, p. 129.

|| Ann. der Chem. u. Pharm. Vol. 49, p. 261.

¶ Journ. für prakt. Chem. Vol. 36, p. 183.



(Gov. Kaluga), and Grigorjewa (Gov. Rjasan); by Woskressensky. According to Murchison,\* from the old coal formation :

Carbon.		Hydrogen.		Oxygen and Nitrogen.		Earthy substances.	
Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
79·3	67·9	6·1	3·6	26·0	15·5	26·0	2·7

XIV. Analyses of a large number of North American coals, by Johnson,† from the old coal-formation :

A, from Maryland and Pennsylvania.										
76·7	68·4								14·0	7·0
B, from Virginia.										
68·0	53·0								14·0	8·0

XV. Analyses of the best kinds of coal and lignite of Hungary ; by Nendtwich :‡

89·9	67·3		6·0	4·3					12·0	0·8
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XVI. Analyses of lignite from Uttweiler (a), north of the Siebengebirge, and fossil wood from Brühl (b) ; by Karsten :§

(a) 77·9		2·6		19·5		1·0
(b) 64·1		5·0		30·9		14·3

XVII. Analyses of lignite from Sipplingen ; by L. Gmelin :||

70·2		3·7		26·1		5·5
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XVIII. Analyses of four perfect lignites from the mouth of the Rhone, of Dax, Lower Alps, and Meissner (pitch coal) ; by Regnault:¶

74·2	72·2		5·9	4·9		22·5	20·1		13·4	1·8
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XIX. Analyses of eight lignites, from Meissner (pitch coal, and coal intermediate between it and lignite), from Hirschberg and Habichtswald (pitch coal and columnar coal), from Ringenkuhl and Stillberg, on the Söhrwald ; by Kühnert :\*\*

73·9	63·5		6·0	4·9		31·6	20·7		7·0	0·8
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\* The Geology of Russia, p. 101 and 78.

† A report on American coals, 1844. As I am acquainted with this report only in the form of an abstract, I do not know whether the per-centage of carbon given is after deduction of the earthy constituents, or not.

‡ Journ. für prakt. Chemie. Vol. 41, p. 8.

§ Loc. cit.

|| Jahrbuch für Mineralogie, &c. 1849, p. 527.

¶ Loc. cit.

\*\* Ann. de Chem. u. Pharm. Vol. 37, p. 94.

XX. Analyses of six specimens of lignite from Meissner (black and brown lignite), Hirschberg (glance coal and brown coal), Fahlbach (black coal), and Mühlhausen (lignite); by Gräger :\*

Carbon.		Hydrogen.		Oxygen and Nitrogen.		Earthy substances.	
Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
75·1	68·6	8·3	5·9	25·1	19·0	47·2	2·3

XXI. Analysis of stangen and glance coal from Meissner; by Kühnert and Gräger :†

86·6		4·0		9·4		15·5
89·0		4·6		6·4		4·0

XXII. Analyses of three imperfect lignites from Greece, Cologne, and Usnach; by Regnault :‡

67·3	57·3		5·8	5·3		36·9	27·2		9·0	2·2
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XXIII. Analyses of four specimens of brown coal from Brennerg, near Oedenburg, in Hungary; by Nendtwich :§

72·5	71·0		5·2	4·7		24·5	22·3		2·6	2·1
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XXIV. Analysis of brown coal from Tiflis; by Woskresensky :||

65·6		5·9		28·5		3·0
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XXV. Analysis of brown-coal from Rauen; by Baer :¶

66·1		5·1		28·9		10·7
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XXVI. Analysis of lignite from Bovey Heathfield; by Vaux :\*\*

67·9		5·8		24·0		
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XXVII. Analyses of brown-coal from Oberhart, near Glognitz, with very beautiful ligneous structure; by Schrötter :††

59·2		5·9		34·9		2·6
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XXVIII. Analyses of two lignites, passing into mineral resin, from Ellenbogen and Cuba; by Regnault :‡‡

79·0	77·6		7·9	7·6		14·5	13·5		5·0	3·9
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\* Ibid. Vol. 48, p. 314. Gräger found this coal to contain from 0·7 to 0·8 per cent. of sulphur.

† Loc. cit.

‡ Ibid.

§ Journ. für. prakt. Chem. Vol. 42, p. 365.

|| Loc. cit.

¶ Ibid.

\*\* Loc. cit. This lignite contained 9·4 per cent. sulphur.

†† Poggend. Annal. Vol. 59, p. 37.

‡‡ Loc. cit.

## XXIX. Analysis of asphaltum from Mexico ; by Regnault :

Carbon.		Hydrogen.		Oxygen and Nitrogen.		Earthy substances.	
Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
81.5		9.6		9.0		2.8	

## XXX. Analysis of turf from Vulcaire, Long, Champs-du-Feu ; by Regnault :\*

61.1	60.4		6.5	6.0		33.6	32.5		5.6	4.6
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## XXXI. Analysis of turf from St. Petersburg ; by Woskresensky :†

41.6			4.0			54.4			6.0	
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## XXXII. Analysis of turf from Princetown, near Tavistock ; by Vaux :‡

60.0			6.0			33.8			10.0	
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## XXXIII. Analysis of peat charcoal from Westphalia ; by Baer :§

80.7			4.1			15.2				
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## Coals from II to XIV :||

90.6	74.0		7.2	4.5		20.0	4.4		35.5	0.24
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## Mean of the results of these 67 analyses :

82.1			5.5			12.4				
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## Mean of the results of 59 analyses of coal (II to XI, with the exception of IV and XI) from the younger coal beds :

82.6	<sup>per</sup>		5.6			11.8				
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## Mean of the results of 8 analyses of coal, IV and XI, from the younger coal beds :

80.2			5.0			19.8				
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## Lignites from XVII to XX :

75.1	63.5		8.3	4.9		31.6	19.0		47.2	0.3
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## Columnar and glance coal, XXI :

89.0	86.6		4.6	4.0		9.4	6.4		15.5	4.0
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## Lignite passing into mineral resin and asphalt, XXVIII and XXIX :

81.5	77.6		9.6	7.6		14.5	9.0		5.0	2.8
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## Imperfect lignites, XXII :

67.3	57.3		5.9	5.3		36.9	27.2		10.7	2.2
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## Mean composition of wood :

49.1			6.3			44.6				
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\* Loc. cit.

† Ibid.

‡ Loc. cit. This turf contains 0.6 per cent. sulphur.

§ Loc. cit.

|| The quantity of hydrogen in I is certainly too small, and that of carbon

It follows from the above analyses, that there is no great difference in composition between the coal of older, and that of the younger coal formations. The maximum and minimum of organic constituents would undoubtedly not be so different if there were not so many sources of error in the mode of analysis. The great differences between the quantities of oxygen, which can only be owing to the cause mentioned (p. 261), prove this. The very close correspondence in the composition of the coals V, although the quantities of earthy substances vary greatly, is very interesting; for it shows that, under circumstances otherwise similar, the conversion of vegetable substances into coal takes place in the same way, whether they are mixed with much or little earthy matter.

The composition of brown-coal differs from that of coal, inasmuch as there is a smaller proportion of carbon and a larger proportion of oxygen. The maximum of carbon in brown-coal does not amount to as much as the minimum in coal; and the minimum of oxygen in the former is somewhat greater than the maximum in the latter. In the imperfect brown-coals, which possess a ligneous structure, the percentage of carbon is still smaller, and that of oxygen greater. Their composition, therefore, approaches more to that of perfect wood. The columnar and glance coal, from Meissner, are an exception to this rule. Their composition is precisely the same as that of coal. On the contrary, that of the glance coal from Hirschberg is intermediate between those of coal and brown-coal. These coals are at both places in contact with basalt, and on this account they are regarded as brown-coal altered by heat.\* Their small percentage of oxygen appears to favour such a view.

The lignites passing into mineral resin and asphalte, differ essentially from coal and brown coal, by containing a larger percentage of hydrogen.

Karsten† and Regnault found that the ash of coal seldom con-

too large. The unusually large quantities of oxygen in XI and XII admit of the conjecture that the coals contained chemically combined water. At least, there are no grounds for assuming that the Russian coals differ so much in composition from the other varieties.

\* Leonhard, *die Basalt-Gebilde*. Abth. II, p. 286, &c.

† Karsten found the ash of coal from Wettin and Löbejün to contain 24·3 to 26·4 per cent. lime, partly combined with carbonic acid. Limestone beds overlie these coal beds. In fissures of the coal there occur iron pyrites, copper pyrites, galena, blende, quartz, calc-spar, and heavy-spar. In the fissures perpendicular or nearly so to the planes of stratification in the coal beds of Saarbrücken, dolomite often occurs. In the coal beds of Minden, a mass occurs in



tained any considerable quantity of lime. The ashes of the coals analysed by Richardson did not show the slightest effervescence with acids, nor did they contain a trace of sulphuric acid. The examination of coal itself with acids, in order to detect the presence of carbonates, although greatly to be desired, has seldom been made. The ash of coal consists chiefly of very finely divided argillaceous particles disseminated throughout the entire mass, and containing water, which is not expelled except by a red heat. When the ash is very ferruginous, the coals generally contain much iron pyrites. Vaux frequently found them to contain traces of copper and lead, and Daubree\* arsenic and antimony.

Baert† found that the principal substances in the ashes of the coals examined by him were peroxide of iron, alumina, lime, silica, sulphuric acid, and sulphur. He found baryta in very much smaller quantity (only in Silesian coals), magnesia, chlorine, and phosphoric acid. In those ashes which contained only a small percentage of peroxide of iron, alumina preponderated; in others the quantities of both were nearly equal. On the addition of hydrochloric acid, more or less sulphuretted hydrogen was disengaged.

We are indebted to Kremers for more accurate examinations of the earthy constituents of coal and brown-coal.‡ He selected for this purpose such specimens as showed under the microscope distinct vegetable cells or ligneous structure.

	I.	II. <i>a</i>	II. <i>b</i>	III.	IV.	V.
Silica ....	15.48	45.13	60.23	31.30	1.70	3.12
Alumina ....	5.28	22.47	31.63	8.31	2.12	29.50
Peroxide of iron ....	74.02	25.83	6.36	54.47	60.79	32.78
Lime ....	2.26	2.80	1.08	3.44	19.22	20.56
Magnesia ....	0.26	0.52	0.35	1.60	5.03	2.16
Potash ....	0.53	0.60	0.11	0.07	0.35	0.99
Soda ....	—	0.28	—	0.29	0.08	1.72
Sulphate of lime ....	2.17	2.37	0.24	0.52	10.71	9.17
	101.53	100.60	98.37	98.95	99.30	100.00
Percentage of ash ....	1.99	1.89	1.74	11.18	3.06	1.16

I. Glance coal from Oberndorf, near Zwickau, of homogeneous character.

the fissures, consisting of carbonates of lime, protoxide of iron, magnesia, and protoxide of manganese, amounting to at least one-third of the coal.

\* Comptes rendus. Vol. 27, p. 827.

† Loc. cit.

‡ Ibid.

## II. Coal from Zwickau, consisting of alternating seams.

a. Compact glance-coal.

b. Porous soot-coal (russkohle).

## III. Coal from Waldenburg.

## IV. Coal from the coal-beds of the Inde.

## V. Brown-coal from Artern.

Of phosphoric acid, which was certainly present originally, but which has hitherto not been detected by analysis, only minute traces were found; and of the alkalis the quantities stated.

Kremers infers from these analyses, that the inorganic constituents which were originally present in the vegetable substances from which coal has been formed, have been replaced by others.\*

It is to be supposed, that coals containing such large quantities of lime as in IV and V, have been produced from water-plants (p. 259).

H. Taylor† has carried out a valuable series of analyses of the earthy constituents of coal, and the strata alternating with the coal beds in the Newcastle coal basin. The strata succeed each other in the following order, from the underlying to the overlying:

	I.	II.	III.	IV.	V.
Silica .....	62.44	59.56	64.21	56.51	58.99
Alumina .....	31.22	12.19	28.78	31.89	26.19
Peroxide of iron .....	2.26	15.96	2.27	—	5.14
Protoxide of iron .....	—	—	—	7.04	5.11
Lime .....	0.75	9.99	1.34	1.69	0.67
Magnesia .....	0.85	1.13	1.12	0.85	1.54
Potash .....	2.48	1.17	2.28	1.38	2.34
Soda....	0.00	—	—	0.61	—
	100.00	100.00	100.00	99.97	99.98

I. Fire-clay, generally immediately beneath the coal strata; after deducting 10.5% water, and 0.44% chloride of sodium and sulphate of soda.

II. Ash of good coal (1.36%), after deducting 8.2% sulphuric acid.

III. Ash of impure coal (16.9%), after deducting sulphuric acid.

IV. Bituminous shale clay, after deducting 39.35% organic matter.

V. Bluish shale clay, after deducting 11.0% water.

The total difference between the earthy substances of the coals

\* Loc. cit.

† Ibid.

II and III, and the inorganic substances of plants, together with their close correspondence with the surrounding clay and slate beds, I, IV, and V, shows that they, as well as the latter, are of sedimentary origin. The composition of the earthy part of the coal does not vary more than the composition of the clay and shale; it is only the percentage of peroxide of iron and lime in II which preponderates. Kremers' analyses show in almost every case a preponderance of iron. However, as in augite, hornblende, &c., in crystalline and sedimentary rocks, peroxide of iron and alumina mutually represent each other; in the earthy part of coal, the percentage of one increases as the other diminishes.

The resemblance between the compositions of the earthy part of coal, and the strata alternating with those of coal, is also observable in Kremers' analyses. The composition of II *b* precisely resembles that of fire-clay and shale. However, the other ashes differ greatly from any sedimentary rocks hitherto analysed. It is, therefore, greatly to be desired that he may continue his careful investigation of the strata associated with the coal whose ashes he has analysed.

As the composition of the organic part of the bituminous shale, IV, very nearly corresponds with that of coal, and it differs from this only in containing a larger percentage of ash, Taylor infers, that both have been formed under similar circumstances; I would myself be more inclined to say from the same materials, but in inverse proportion.

The results of Kremers and Taylor's investigations can only be explained by assuming that there was an intimate mixture of vegetable and earthy substances. This may have taken place when plants, such as calamites, were so porous as to admit of the penetration of the suspended matter of sea-water into their cells, or in consequence of the previous fine division of the plants by decay. Coal, when produced by the former process, would still retain distinct vegetable cells and ligneous structure; but when produced by the latter process, this structure might even be visible, as in decayed wood. Compact woods admit of the penetration of water and deposition of dissolved substances in the interior, but the suspended matter of water cannot be introduced until after the partial destruction of the woody tissues. Consequently coals which, like those examined by Kremers and Taylor, contain the constituents of the strata associated with them, cannot have been formed from compact wood without previous decay having taken place.

According to De Saussure, 240 parts of dry oak shavings convert 10 cubic inches of oxygen into an equal volume of carbonic acid, containing 3 parts by weight of carbon. The weight of the shavings, however, is diminished by 15 parts; consequently 12 parts of water have likewise been separated from the elements of wood. Liebig\* observed that shavings of wood taken from the tree, at first reduced the volume of oxygen, while moistened wood, which had been for some time exposed to the action of the atmosphere, converted oxygen into carbonic acid without reduction of volume. The absorption of oxygen in the former case would therefore appear to be owing not to the woody fibre, but to the soluble nitrogenous substances contained in the wood, which are extracted by water, and whose elements are entirely oxidized. That such an extraction takes place is sufficiently proved by the presence of organic matter in all water, the baregin and the crenic acid in the water of springs, the latter of which passes under the influence of the atmosphere into the sparingly soluble apocrenic acid.

But even the oxidation of the carbon in wood must have its limits, otherwise wood exposed to atmospheric influence would ultimately disappear, with the exception only of the mineral constituents. All our experience, however, shows that such is never the case.

In considering the subject of the conversion of vegetable remains into coal and brown coal, I shall in all instances assume that ligneous tissues have been principally concerned in this change; an assumption which is the more justified by the great probability that forest trees at all times constituted the chief part of the vegetation of the ancient world.†

From the comparison of the composition of brown decayed oak and beech wood with that of these woods in a perfect state, Liebig‡ infers, that in the decay of ligneous tissues the oxygen of the atmosphere does not combine with the carbon, but only with the hydrogen, which is thus separated, and that the carbonic acid generated at the same time is derived altogether from the elements of wood. He also infers from the composition of a specimen of white rotten wood from the interior of a dead tree, that in this change the elements of water, together with a certain quantity of

\* Die Chemie in ihrer Anwendung auf Agricultur, 6te Aufl. p. 477, et seq.

† Unger. loc. cit. p. 273.

‡ Loc. cit. p. 477.



oxygen, enter into combination with the wood, while carbon and oxygen are separated as carbonic acid.

There is no doubt that organic substances lying under water are subject to oxidation by the absorbed atmospheric air, in the same way that mineral substances, such as protoxide of iron, are oxidized under similar circumstances. This change may possibly go on even at very great depths beneath the surface of the sea, for water taken from a depth of 2243 feet was found to contain oxygen (p. 114).\* Göppert† found that mosses lying 6 or 8 inches under water were decomposed very rapidly, and at a depth of 12 to 36 inches were tolerably well preserved for 15 months. It appears from this, that the decomposition of vegetable substances under water goes on more slowly the deeper they are beneath the surface, owing, probably, to the slower replacement at these depths of the oxygen consumed in their decay. In any case, the decomposition of these substances may assume different characters, according as it takes place in waters of greater or less depth.

Coal sometimes contains as much hydrogen as ligneous fibre, and sometimes only  $1\cdot8\frac{0}{0}$  less; the oxygen, on the contrary, amounts in the former to  $26\frac{0}{0}$ , or  $40\frac{0}{0}$  less than in the latter. Consequently, in the conversion of wood into coal, there must be an essential loss of oxygen by the former, by which the relative quantities of hydrogen and carbon are increased. The principal question is, as to how the oxygen has been separated; whether in combination with hydrogen as water, or with carbon as carbonic acid. If, as Liebig considers, atmospheric oxygen unites only with the hydrogen of the wood, the oxygen can only be separated in combination with carbon. There are no reasons for supposing that sea-water does not contain absorbed oxygen even at depths still greater than 2243 feet; but if we imagine vegetable substances sunk to very great depths, where neither the motion of waves nor currents tend to replace the consumed oxygen, it becomes difficult to understand how a continuous oxidation of their hydrogen should be effected. We must therefore examine whether such an oxidation is a condition necessary to the conversion of these substances into coal. De Saussure's experiments prove that hydrogen and oxygen are

\* According to A. Hayes (p. 103). Sea-water exercises the most powerful oxidizing influence at the surface; for instance, upon the copper sheathing of vessels. At a considerable depth, on the contrary, copper, bronze, silver, and brass are covered with a crust of sulphurets. Since then the sulphates contained in sea-water are deoxidized by organic substances below a certain depth, it is not very probable that oxidation can go on at the same time.

† Poggendorff's Ann. Vol. 86, p. 484.

evolved from the elements of wood. Carburetted hydrogen and carbonic acid escape from bogs where organic substances are undergoing decay, but it has not yet been decided whether or not carburetted hydrogen is disengaged in the decay of wood. If water is a condition of this evolution, it may be expected to take place in hollow trunks of trees, for the decayed wood which they contain is always moist and pasty, not unfrequently covered by rain-water to a depth of several feet. The presence of hydrocarbons in the atmosphere, proved by Boussingault, show that processes of decomposition go on which supply these substances.

It is in the highest degree probable that the formation of carburetted hydrogen from organic substances is connected with the limited access of atmospheric oxygen to them; and it is, therefore, more especially to be expected when the decomposition goes on under water, as in marshes and bogs. Under these circumstances a portion of the hydrogen is always disengaged in combination with carbon. The very frequent exhalations of carbonic acid and carburetted hydrogen in the coal basins shows that there is a continuous separation of oxygen and hydrogen, in combination with carbon, from coal (p. 253). This circumstance accounts for the different percentage of oxygen and hydrogen in coal, the proportions of which determine the quantity of volatile substances which they yield.\* This separation of oxygen and hydrogen takes place not

\* The investigations of Regnault and Vaux show that the quantity of coke which coal affords is very nearly in direct proportion to the quantity of carbon they contain, and inversely as to that of their oxygen. The varieties of brown coal present the same relations, although with less uniformity. The quantity of hydrogen in coal and brown coal, which upon the whole varies much less than those of oxygen, appears to have no influence upon the quantity of non-volatile products. However, lignites rich in hydrogen and passing into the state of mineral resin, as well as asphalte, yield the smallest quantity of coke, and the largest of volatile products. Therefore a continuous evolution of carbonic acid and carburetted hydrogen from coal, lessens the quantity of volatile products. Every circumstance which favours this evolution, favours also the diminution of these products. The proportion of volatile products varies from a nearly total deficiency in the driest anthracites, to an abundance, which amounts, in the richest coking coal, to 50 per cent. W. B. Rogers and H. D. Rogers (Reports of the Association of American Geologists, &c. Boston, 1843, p. 470) have found, as the result of numerous analyses, that in the Appalachian coal strata the proportion of volatile matter is smaller, the more the coal fields are disturbed, and associated with flexures and dislocations. They were able, in more than one instance, to trace the same coal seam through its various degrees of bituminization, from an almost true anthracite to a state in which it possesses a full proportion of volatile matter. The cause of the different degrees of de-bituminization of the coal in different parts of their range, B. Rogers is disposed to attribute to the prodigious quantity of intensely heated steam and gaseous matter emitted through the crust of the earth by the almost infinite number of cracks and crevices, which must have been produced by the undulation and permanent bending of the strata. He states that the

only from the coal itself, but likewise from strata associated with it, when they contain much organic matter. This is shown by the immense exhalations of carburetted hydrogen from an artesian well, mentioned at p. 256: for by boring to a depth of 80 to 242 feet below the worked coal seams,\* no other seam was found.

The frequent evolution of carburetted hydrogen, mixed with more or less carbonic acid, from ascending springs and artesian wells, is evidence in favour of the opinion that these gases come from a region where coal or organic substances are in contact with water. The circumstance that the evolution of combustible gas in coal mines frequently increases with the depth, is no less in favour of this view, for the quantity of water entering the mines generally increases with the depth. Morand† has already noticed that the mines where the quantity of water is great, are apparently rich in explosive gas. It is, therefore, probable that carburetted hydrogen is generated only where vegetable substances are decomposed under water. If the presence of water determines the evolution of combustible gas, this will account for its absence in brown coal mines (p. 253), the beds in which seldom extend below the bottom of the valleys.‡

According to Liebig's view, the conversion of ligneous fibre into coal consisted in the separation of certain quantities of its elements in the form of oils, marsh gas, and carbonic acid. When from the formula representing the composition of wood there are deducted 3 equivalents of marsh gas, 3 equivalents of water, and 9 equivalents of carbonic acid, there remain the constituents of splint coal of Newcastle, and the cannel coal of Lancashire.

On comparing the composition of brown-coal, from Laubach, in the Wetterau, with that of oak wood, Liebig found that the former might be produced from the latter by the separation of 2

coal, if thus effectually steamed and raised in temperature in every part of its mass, would discharge a greater or less proportion of its bitumen, and other volatile constituents. My own view, which is founded upon a fact relating to the generation of carburetted hydrogen and carbonic acid, appears to render such an artificial hypothesis unnecessary. The smaller quantity of volatile substances in the disturbed coal fields may be connected with the more ready access of water, which favoured the evolution of those gases.

\* See my prize essay, "Sur l'aérage des mines," in "Des Moyens de soustraire l'exploitation des mines de houille aux changes d'explosion." Bruxelles, 1840, p. 236.

† *L'art d'exploiter les mines de charbon de terre.* 1768. Vol. 1, p. 38.

‡ Lyell's statement (Second Journey to North America, Vol. 2) that at the mouth of the Mississippi, where a large quantity of driftwood is annually buried in mud and sand, carburetted hydrogen is exhaled everywhere from the ground, shows evidently that the presence of water determines its exhalation.

equivalents of hydrogen and 3 equivalents of carbonic acid. As regards the formation of the brown-coal of Ringkuhl, it may be assumed that besides hydrogen and the elements of carbonic acid, those of water were also separated from the ligneous fibre.

Göppert states that the timber in the coal mines at Charlottenbrunn is sometimes converted into brown-coal. The same conversion was many years ago found in an old gallery of an iron mine at Turrach, in Steria. A. Schrötter explains, according to the analysis made by him, this conversion, by the separation of marsh gas and carbonic acid from the ligneous fibre of oak wood.\*

In all the previous endeavours to explain the conversion of wood into coal or brown-coal as consisting in the separation of binary compounds of the elements, the subject was regarded only from one point of view. The formulæ which have thus been developed have, consequently, no value. Keeping out of view olefiant gas and the non-gaseous compounds of carbon with hydrogen, there remain only carbonic acid, carburetted hydrogen, and water, by the separation of which from wood the explanation of its conversion into coal can be sought for. The partial separation of oxygen, hydrogen, and carbon from wood, as water and carbonic acid, is an established fact. So likewise is the separation of hydrogen and carbon as carburetted hydrogen, at least when the decomposition takes place under water.

This conversion of wood into coal may take place in four different ways, namely:

1. By the separation of carbonic acid and carburetted hydrogen.
2.   "               "               carbonic acid and water.
3.   "               "               carburetted hydrogen and water.
4.   "               "               carbonic acid, carburetted hydrogen, and water.

The second kind of decomposition may be supposed to consist in the formation of water, either solely from the hydrogen and oxygen of the wood, or in the oxidation of a part or the whole of the hydrogen by external oxygen. The progressive increase of carbon during the change, proves that no direct oxidation of carbon by external oxygen takes place. The third mode of decomposition cannot be supposed to occur, because carburetted hydrogen is never disengaged without carbonic acid.

I have constructed formulæ which represent the three following modes of the formation of coal.

\* Unger, loc. cit. p. 92.



I. By the separation of carbonic acid and carburetted hydrogen.

II. By the separation of carbonic acid from the elements of wood, and by the oxidation of hydrogen by external oxygen.

III. By the separation of carbonic acid and water from among the elements of wood.

These three cases belong to the definite problems, for which formulæ may be constructed. The case in which carbonic acid, carburetted hydrogen, and water are separated, is an indefinite problem which admits of several solutions. Among the possible modes in which the change may take place, there is none in which a larger quantity of carbon is separated from the wood, and lost, than in the first of the above cases; and, on the other hand, none in which less is lost than in the third case. This loss of carbon approaches nearer to the maximum the greater the quantity of carburetted hydrogen mixed with the disengaged water and carbonic acid, and nearer to the minimum in the opposite case.

If the quantities of the elements are represented—

	In wood.		In coal, or any product of the alteration of wood.
Carbon	. = $a$	.	= $\alpha$
Hydrogen	. = $b$	.	= $\beta$
Oxygen	. = $c$	.	= $\varepsilon$

and if in the first-mentioned case  $x$  = the oxygen, and  $y$  = the hydrogen which must be separated, we have then the following proportions:—

$$a - 0.375 x - 3y : b - y : c - x = \alpha : \beta : \varepsilon.$$

Hence it follows that,

$$x = \frac{(\alpha - 3\beta) c - (a - 3b) \varepsilon}{\alpha - 0.375 \varepsilon - 3\beta}$$

$$y = \frac{(x - c) \beta + \varepsilon b}{\varepsilon}$$

If, in the second case,  $x$  = the oxygen which is disengaged in combination with the carbon, and  $y$  = the hydrogen oxidized by external oxygen, we obtain the proportions,

$$a - 0.375 x : b - y : c - x = \alpha : \beta : \varepsilon.$$

Hence it follows that,

$$x = \frac{\alpha c - \varepsilon a}{\alpha - 0.375 \varepsilon}$$

$$y = \frac{(x - c) \beta + \varepsilon b}{\varepsilon}$$

If, in the third case,  $x$  = the oxygen disengaged in combination with carbon, and  $y$  = the hydrogen disengaged in com-

bination with oxygen derived from the wood, we have the proportions :

$$a - 0.375 x : b - y : c - 8.01 y - x = \alpha : \beta : \varepsilon ;$$

consequently,

$$y = \frac{0.375 (\beta c - \varepsilon b) + \alpha b = \beta a}{3 \beta - 0.375 \varepsilon + \alpha}$$

$$x = \frac{\beta a - \alpha (b - y)}{0.375 \beta} *$$

From the above six equations, the following values for  $x$  and  $y$  are obtained.

### 1. Coal; mean of 67 analyses :

I. $x = 41.9.$				$y = 5.09.$	
	Wood.			Coal.	Percentage.
Carbon	....	49.1	— 31.0	= 18.1	82.2
Hydrogen	....	6.3	— 5.1	= 1.2	5.5
Oxygen	....	44.6	— 41.9	= 2.7	12.3
		<hr/> 100.0	<hr/> 78.0	<hr/> 22.0	<hr/> 100.0

57.6 per cent. carbonic acid and 20.4 carburetted hydrogen are disengaged.

II. $x = 39.45.$				$y = 4.01.$	
Carbon	...	49.1	— 14.80	= 34.30	82.2
Hydrogen	....	6.3	— 4.01	= 2.29	5.5
Oxygen	....	44.6	— 39.45	= 5.15	12.3
		<hr/> 100.0	<hr/> 58.26	<hr/> 41.74	<hr/> 100.0

54.24 per cent. carbonic acid is disengaged, and 4.01 per cent. hydrogen oxidized.

III. $x = 11.41.$				$y = 3.31.$	
Carbon	....	49.1	— 4.3	= 44.8	82.2
Hydrogen	....	6.3	— 3.3	= 3.0	5.5
Oxygen	....	44.6	— 37.9	= 6.7	12.3
		<hr/> 100.0	<hr/> 45.5	<hr/> 54.5	<hr/> 100.0

15.7 per cent. carbonic acid and 29.8 per cent. water are disengaged.

The wood, therefore,

	lost	and	yielded
In I.	78.0 per cent.		22.0 per cent. coal.
„ II.	58.3 „		41.7 „ „
„ III.	45.5 „		54.5 „ „

\* The value of  $x$  may be determined more simply from this equation than when the value of  $y$  was substituted in it.

## 2. Coal; mean of 49 analyses :

I. $x = 42.02$ . $y = 5.07$ .				
	Wood.		Coal.	Percentage.
Carbon	.... 49.1	— 30.97	= 18.13	82.6
Hydrogen	.... 6.3	— 5.07	= 1.23	5.6
Oxygen	.... 44.6	— 42.02	= 2.58	11.8
	100.0	78.06	21.94	100.0

57.78 per cent. carbonic acid and 20.28 per cent. carburetted hydrogen are disengaged.

II. $x = 39.73$ . $y = 3.98$ .				
Carbon	.... 49.1	— 14.90	= 34.20	82.6
Hydrogen	.... 6.3	— 3.98	= 2.32	5.6
Oxygen	.... 44.6	— 39.73	= 4.87	11.8
	100.0	58.61	41.39	100.0

54.63 per cent. carbonic acid is disengaged, and 3.98 per cent. hydrogen oxidized.

III. $x = 12.15$ . $y = 3.28$ .				
Carbon	.... 49.1	— 4.56	= 44.54	82.9
Hydrogen	.... 6.3	— 3.28	= 3.02	5.6
Oxygen	.... 44.6	— 38.42	= 6.18	11.5
	100.0	46.26	53.74	100.0

16.71 per cent. carbonic acid and 29.55 per cent. water are disengaged.

## 3. Coal from the Marennen.\*

I. $x = 40.1$ . $y = 5.0$ .				
Carbon	.... 49.1	— 30.0	= 19.1	76.7
Hydrogen	.... 6.3	— 5.0	= 1.3	5.2
Oxygen	.... 44.6	— 40.1	= 4.5	18.1
	100.0	75.1	24.9	100.0

55.1 per cent. carbonic acid and 20.0 per cent. carburetted hydrogen are disengaged.

II. $x = 36.25$ . $y = 3.84$ .				
Carbon	.... 49.1	— 13.6	= 35.5	76.7
Hydrogen	.... 6.3	— 3.8	= 2.5	5.3
Oxygen	.... 44.6	— 36.3	= 8.3	18.0
	100.0	53.7	46.3	100.0

49.8 per cent. carbonic acid is disengaged, and 3.8 per cent. hydrogen oxidized.

III. $x = 8.8$ . $y = 3.13$ .				
Carbon	.... 49.1	— 3.30	= 45.8	76.7
Hydrogen	.... 6.3	— 3.10	= 3.2	5.3
Oxygen	.... 44.6	— 33.90	= 10.7	18.0
	100.0	40.30	59.7	100.0

12.1 per cent. carbonic acid and 28.2 per cent. water are disengaged.

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\* However, it is said that this coal is a tertiary formation. In this case, the composition of this brown-coal approaches that of the proper coal more than any other brown-coal.

## 4. Anthracite, from Lamure, according to Regnault :

I.  $x = 43.95.$        $y = 6.03.$

		Wood.		Anthracite.	Percentage.
Carbon	....	49.1	—	34.57 = 14.53	94.04
Hydrogen	....	6.3	—	6.03 = 0.27	1.75
Oxygen	....	44.6	—	43.95 = 0.65	4.21
		100.0		84.55	100.0
				15.45	

60.79 per cent. carbonic acid and 24.12 per cent. carburetted hydrogen are disengaged.

II.  $x = 43.12.$        $y = 5.7.$

Carbon	....	49.1	—	16.17 = 32.93	94.06
Hydrogen	....	6.3	—	5.7 = 0.60	1.71
Oxygen	....	44.6	—	43.12 = 1.48	4.23
		100.0		64.99	100.0
				35.01	

59.29 per cent. carbonic acid is disengaged, and 5.7 per cent. hydrogen oxidized.

III.  $x = -0.375.$        $y = 5.38.$

Since  $x$  has here a negative value, the conversion of wood into anthracite by the mere separation of carbonic acid and water from among its elements, is impossible. Consequently, if this conversion took place, a part of the hydrogen must have been separated, either in combination with carbon (I), or by combination with external oxygen (II). In that case, besides carbonic acid and water, only 0.075° per cent. carburetted hydrogen would be disengaged.

## 5. Lignite from the Lower Alps, analyzed by Regnault :

I.  $x = 38.3.$        $y = 4.8.$

		Wood.		Lignite.	Percentage.
Carbon	....	49.1	—	28.8 = 20.3	72.3
Hydrogen	....	6.3	—	4.8 = 1.5	5.3
Oxygen	....	44.6	—	38.3 = 6.3	22.4
		100.0		71.9	100.0
				28.1	

52.7 per cent. carbonic acid and 19.2 per cent. carburetted hydrogen are disengaged.

II.  $x = 32.2.$        $y = 4.2.$

Carbon	....	49.1	—	12.5 = 36.6	72.2
Hydrogen	....	6.3	—	3.6 = 2.7	5.3
Oxygen	....	44.6	—	32.2 = 11.4	22.5
		100.0		49.3	100.0
				50.7	

45.6 per cent. carbonic acid is disengaged, and 4.2 per cent. hydrogen oxidized.



		III. $x = 7.26.$		$y = 2.9.$	
		Wood.		Lignite.	
				Percentage.	
Carbon	....	49.1	— 2.7	= 46.4	72.6
Hydrogen	....	6.3	— 2.9	= 3.4	5.3
Oxygen	....	44.6	— 30.5	= 14.1	22.1
		100.0	36.1	63.9	100.0

10 per cent. carbonic acid and 26.1 per cent. water are disengaged.

## 6. Fossil wood from Usnach, analysed by Regnault :

		I. $x = 25.4.$		$y = 3.25.$	
		Wood.		Fossil wood.	
				Percentage.	
Carbon	....	49.1	— 18.65	= 30.45	57.8
Hydrogen	....	6.3	— 3.25	= 3.05	5.8
Oxygen	....	44.6	— 25.40	= 19.20	36.4
		100.0	47.30	52.70	100.0

34.9 per cent. carbonic acid and 14 per cent. carburetted hydrogen are disengaged.

		II. $x = 17.17.$		$y = 1.95.$	
Carbon	....	49.1	— 6.40	= 42.70	57.3
Hydrogen	....	6.3	— 1.95	= 4.35	5.8
Oxygen	....	44.6	— 17.20	= 27.40	36.9
		100.0	25.55	74.45	100.0

23.6 per cent. carbonic acid is disengaged, and 1.95 hydrogen oxidized.

		III. $x = 2.62.$		$y = 1.39.$	
Carbon	....	49.1	— 1.00	= 48.10	57.3
Hydrogen	....	6.3	— 1.40	= 4.90	5.9
Oxygen	....	44.6	— 13.75	= 30.85	36.8
		100.0	16.15	83.85	100.0

3.6 per cent. carbonic acid and 12.5 per cent. water are disengaged.

## 7. Lignite passing into mineral resin, analysed by Regnault:

		I. $x = 40.58.$		$y = 4.1.$	
		Wood.		Lignite.	
				Percentage.	
Carbon	....	49.1	— 27.5	= 21.6	77.6
Hydrogen	....	6.3	— 4.1	= 2.2	7.9
Oxygen	....	44.6	— 40.6	= 4.0	14.5
		100.0	72.2	27.8	100.0

55.8 per cent. carbonic acid and 16.4 per cent carburetted hydrogen are disengaged.

		II. $x = 38.08.$		$y = 2.78.$	
Carbon	....	49.1	— 14.3	= 34.8	77.7
Hydrogen	....	6.3	— 2.8	= 3.5	7.8
Oxygen	....	44.6	— 38.1	= 6.5	14.5
		100.0	55.2	44.8	100.0

52.4 per cent. carbonic acid is disengaged, and 2.78 per cent. hydrogen oxidized.

III.  $x = 20.05$ . $y = 2.1$ .

	Wood.		Lignite.	Percentage.
Carbon	.... 49.1	— 7.5	= 41.6	77.8
Hydrogen	.... 6.3	— 2.1	= 4.2	7.8
Oxygen	.... 44.6	— 36.9	= 7.7	14.4
	100.0	46.5	53.5	100.0

27.6 per cent. carbonic acid and 18.9 per cent. water are disengaged.

## 8. Turf, from Princetown, analysed by Vaux :

I.  $x = 29.08$ . $y = 3.54$ .

	Wood.		Turf.	Percentage.
Carbon	.... 49.1	— 21.5	= 27.6	60.1
Hydrogen	.... 6.3	— 3.5	= 2.8	6.1
Oxygen	.... 44.6	— 29.1	= 15.5	33.8
	100.0	54.1	45.9	100.0

40 per cent. carbonic acid and 14.2 per cent. carburetted hydrogen are disengaged.

II.  $x = 21.5$ . $y = 2.2$ .

Carbon	.... 49.1	— 8.1	= 41.0	60.1
Hydrogen	.... 6.3	— 2.2	= 4.1	6.0
Oxygen	.... 44.6	— 21.5	= 23.1	33.9
	100.0	31.8	68.2	100.0

29.6 per cent. carbonic acid is disengaged, and 2.2 per cent. hydrogen oxidized.

III.  $x = 5.33$ . $y = 1.6$ .

Carbon	.... 49.1	— 2.00	= 47.10	60.2
Hydrogen	.... 6.3	— 1.60	= 4.70	6.0
Oxygen	.... 44.6	— 18.15	= 26.45	33.8
	100.0	21.75	78.25	100.0

7.33 per cent. carbonic acid and 14.42 per cent. water are disengaged.

## 9. Peat coal, analysed by Baer :

I.  $x = 41.34$ . $y = 5.41$ .

	Wood.		Peat coal.	Percentage.
Carbon	.... 49.1	— 31.73	= 17.37	80.7
Hydrogen	.... 6.3	— 5.41	= 0.89	4.1
Oxygen	.... 44.6	— 41.34	= 3.26	15.2
	100.0	78.48	21.52	100.0

56.84 per cent. carbonic acid and 21.64 per cent. carburetted hydrogen are disengaged.

II.  $x = 38.06$ . $y = 4.53$ .

Carbon	.... 49.1	— 14.27	= 34.83	80.7
Hydrogen	.... 6.3	— 4.53	= 1.77	4.1
Oxygen	.... 44.6	— 38.06	= 6.54	15.2
	100.0	56.86	43.14	100.0

52.33 per cent. carbonic acid is disengaged, and 4.53 per cent. hydrogen is oxidized.

		III. $x = 4.32$ .		$y = 3.89$ .		
		Wood.		Peat coal.		Percentage.
Carbon	....	49.1	— 1.62	=	47.48	80.5
Hydrogen	....	6.3	— 3.89	=	2.41	4.1
Oxygen	...	44.6	— 35.48	=	9.12	15.4
		<hr/> 100.0	<hr/> 40.99		<hr/> 59.01	<hr/> 100.0

5.94 per cent. carbonic acid and 35.05 per cent. water are disengaged.

# 10. Asphalte, analysed by Regnault:

		I. $x = 42.16.$		$y = 3.71.$		
		Wood.		Asphalte.		Percentage.
Carbon	...	49.1	— 26.9	=	22.2	81.6
Hydrogen	...	6.3	— 3.7	=	2.6	9.6
Oxygen	...	44.6	— 42.2	=	2.4	8.8
		<hr/> 100.0	<hr/> 72.8		<hr/> 27.2	<hr/> 100.0

58 per cent. carbonic acid and 14.8 per cent. carburetted hydrogen are disengaged.

		II. $x = 40.88$ .		$y = 2.32$ .		
Carbon	...	49.1	— 15.3	= 33.8		81.5
Hydrogen	...	6.3	— 2.3	= 4.0		9.6
Oxygen	...	44.6	— 40.9	= 3.7		8.9
		100.0	58.5	41.5		100.0

56.2 per cent. carbonic acid is disengaged, and 2.32 per cent. hydrogen oxidized.

		III. $x = 26.63$ .		$y = 1.69$ .		
Carbon	....	49.1	— 10.0	= 39.1		81.5
Hydrogen	....	6.3	— 1.7	= 4.6		9.6
Oxygen	....	44.6	— 40.3	= 4.3		8.9
		<u>100.0</u>	<u>52.0</u>	<u>48.0</u>		<u>100.0</u>

36.62 per cent. carbonic acid and 15.23 per cent. water are disengaged.

Asphalte appears, however, to vary in composition. Bous-singault found a specimen, from Coxitambo, in South America, to consist of 75.0 carbon, 9.5 hydrogen, and 15.5 oxygen.

# 11. Retinite, from the brown-coal mines of Walchow, in Moravia, analysed by Schrötter:

		I. $x = 41.9$ .		$y = 3.09$ .		
		Wood.		Retinite.		Percentage.
Carbon	....	49.1	— 25.0	=	24.1	80.3†
Hydrogen	....	6.3	— 3.1	=	3.2	10.7
Oxygen	....	44.6	— 41.9	=	2.7	9.0
		<hr/> 100.0	<hr/> 70.0		<hr/> 30.0	<hr/> 100.0

57.6 per cent. carbonic acid and 12.4 per cent. carburetted hydrogen are disengaged.

\* Loc. cit.

† The mean of three closely corresponding analyses.

		II. $x = 40.85.$		$y = 1.84.$		
		Wood.		Retinite.		Percentage.
Carbon	...	49.1	— 15.3	= 33.8		80.5
Hydrogen	....	6.3	— 1.8	= 4.5		10.7
Oxygen	....	44.6	— 40.9	= 3.7		8.8
		100.0	58.0	42.0		100.0

56.17 per cent. carbonic acid is disengaged, and 1.84 per cent. hydrogen oxidized.

		III. $x = 29.9.$		$y = 1.29.$		
Carbon	...	49.1	— 11.21	= 37.89		80.2
Hydrogen	....	6.3	— 1.29	= 5.01		10.6
Oxygen	....	44.6	— 40.23	= 4.37		9.2
		100.0	52.73	47.27		100.0

41.11 per cent. carbonic acid and 11.62 per cent. water are disengaged.

## 12. Amber, analysed by Schrötter :

		I. $x = 41.4.$		$y = 3.1.$		
		Wood.		Amber.		Percentage.
Carbon	...	49.1	— 24.8	= 24.3		79.2
Hydrogen	....	6.3	— 3.1	= 3.2		10.4
Oxygen	....	44.6	— 41.4	= 3.2		10.4
		100.0	69.3	30.7		100.0

56.93 per cent. carbonic acid and 12.4 per cent. carburetted hydrogen are disengaged.

		II. $x = 40.07.$		$y = 1.77.$		
Carbon	...	49.1	— 15.0	= 34.1		79.12
Hydrogen	....	6.3	— 1.8	= 4.5		10.44
Oxygen	...	44.6	— 40.1	= 4.5		10.44
		100.0	56.9	43.1		100.0

55.1 per cent. carbonic acid is disengaged, and 1.77 per cent. hydrogen oxidized.

		III. $x = 29.66.$		$y = 1.25.$		
Carbon	...	49.1	— 11.1	= 38.0		79.3
Hydrogen	...	6.3	— 1.3	= 5.0		10.4
Oxygen	....	44.6	— 39.7	= 4.9		10.3
		100.0	52.1	47.9		100.0

40.8 per cent. carbonic acid and 11.3 per cent. water are disengaged.

The above formulæ may likewise be applied to the following analyses. A, decayed oak-wood, from a hollow tree, analysed by Liebig; B, humus from oak wood, analysed by Meyer; C, humus from oak, analysed by Will; D, oak wood, analysed by Gay-Lussac, and Thenard.\*

\* Loc. cit., p. 470.



	A.	B.	C.	D.
Carbon	53.47	54.0	56.0	52.53
Hydrogen	5.16	5.1	4.9	5.27
Oxygen	41.37	40.9	39.1	42.20
	100.0	100.0	100.0	100.0

A.—I.  $x = 3.72$ .  $y = 0.496$ .

	Oak wood.	Decayed wood.	Percentage.
Carbon	52.53	2.88 = 49.65	53.44
Hydrogen	5.27	0.50 = 4.77	5.14
Oxygen	42.20	3.72 = 38.48	41.42
	100.0	7.10	92.90
			100.0

5.12 per cent. carbonic acid and 1.98 per cent. carburetted hydrogen are disengaged.

II.  $x = 2.09$ .  $y = 0.29$ .

Carbon	52.53	0.78 = 51.75	53.44
Hydrogen	5.27	0.29 = 4.98	5.14
Oxygen	42.20	2.09 = 40.11	41.42
	100.0	3.16	96.84
			100.0

2.87 per cent. carbonic acid is disengaged, and 0.29 per cent. hydrogen oxidized.

III.  $x = 0.25$ .  $y = 0.21$ .

Carbon	52.53	0.09 = 52.44	53.63
Hydrogen	5.27	0.21 = 5.06	5.18
Oxygen	42.20	1.93 = 40.27	41.19
	100.0	2.23	97.77
			100.0

0.34 per cent. carbonic acid and 1.89 per cent. water are disengaged.

B.—I.  $x = 5.62$ .  $y = 0.7$ .

	Oak wood.	Humus.	Percentage.
Carbon	52.53	4.21 = 48.32	54.00
Hydrogen	5.27	0.70 = 4.57	5.10
Oxygen	42.20	5.62 = 36.58	40.90
	100.0	10.53	89.47
			100.0

7.73 per cent. carbonic acid and 2.8 per cent. carburetted hydrogen are disengaged.

II.  $x = 3.4$ .  $y = 0.42$ .

Carbon	52.53	1.28 = 51.25	54.0
Hydrogen	5.27	0.42 = 4.85	5.1
Oxygen	42.20	3.40 = 38.80	40.9
	100.0	5.10	94.90
			100.0

4.68 per cent. carbonic acid is disengaged, and 0.42 per cent. hydrogen oxidized.

III.  $x = 0$ .  $y = 0.3$ .

Carbon	52.53	0.0 = 52.53	54.0
Hydrogen	5.27	0.3 = 4.97	5.1
Oxygen	42.20	2.4 = 39.80	40.9
	100.0	2.7	97.30
			100.0

No carbonic acid is disengaged, but 2.7 per cent. of water.

C.—I. $x = 11.7$ .					$y = 1.46$ .	
	Oak wood.				Humus.	Percentage.
Carbon	....	52.53	—	8.77	= 43.76	56.0
Hydrogen	....	5.27	—	1.46	= 3.81	4.9
Oxygen	....	42.20	—	11.70	= 30.50	39.1
		<hr/>		<hr/>	<hr/>	<hr/>
		100.0		21.93	78.07	100.0

16.09 per cent. carbonic acid and 5.84 per cent. carburetted hydrogen are disengaged.

II. $x = 7.57$ .					$y = 0.94$ .	
Carbon	....	52.53	—	2.84	= 49.69	56.0
Hydrogen	....	5.27	—	0.94	= 4.33	4.9
Oxygen	....	42.20	—	7.57	= 34.63	39.1
		<hr/>		<hr/>	<hr/>	<hr/>
		100.0		11.35	88.65	100.0

10.41 per cent. carbonic acid is disengaged, and 0.94 per cent. hydrogen oxidized.

III. $x = 0$ .					$y = 0.69$ .	
Carbon	....	52.53	—	0.00	= 52.53	56.0
Hydrogen	....	5.27	—	0.69	= 4.58	4.9
Oxygen	....	42.20	—	5.53	= 36.67	39.1
		<hr/>		<hr/>	<hr/>	<hr/>
		100.0		6.22	93.78	100.0

6.22 per cent. water is disengaged, but no carbonic acid.

The decayed chocolate-coloured oak wood, A, still presented most perfectly the ligneous structure. Another specimen, of a light brown colour and very friable, gave on analysis 56.211 carbon and 43.789 water, consequently approximating very closely in composition to the humus, C.

This examination of the decay of oak wood, and its conversion into humus, present us with a clear representation of the mode in which coal and brown-coal, &c., are formed by the alteration of ligneous matter. In the former case comparative analyses of the original materials and the products of decomposition may be made, and the process may be traced through its first stages; whereas in the case of coal this is never possible, and in that of brown-coal but seldom.

Even a comparison of the analyses of the unaltered oak wood, and of its products of decomposition, is sufficient to show that the difference in physical characters—cohesion, colour, and structure—is far more considerable than the difference of chemical composition.

When we consider that the loss of substance experienced by the wood varies in III between 2.23 and 6.22 per cent., and even in II is not more than from 3.16 to 11.35 per cent., the maximum loss, of weight in C I, viz., 22 per cent., could not have been reached, even supposing that, besides carbonic acid and water, a small

quantity of carburetted hydrogen may have been disengaged. The considerable decrease in the volume of the wood during its decay is very difficult to account for. It is true that the soluble matter of the wood is carried away at the same time by rain falling into the hollow trees; but as this does not amount on the whole to more than about 4 per cent., its extraction cannot exercise any perceptible influence. Hollow trees are sometimes met with whose wood is entirely decayed away, nothing being left but the bark and a quantity of pulverulent wood, which is altogether disproportionate to the hollow space. In most cases likewise the cavity extends so far below the lateral opening in the trunk, that we cannot suppose the decayed wood to have been washed away by rain, at least not during the last stages of the change. It is, therefore, very desirable that continued careful observations should be made with regard to this point. On the other hand, the slight loss of substance by the wood during the first stages of its decomposition, explain why the alteration of wooden piles under water appears to have taken place without any diminution of volume. If, indeed, besides this, inorganic substances, for instance, silica, should be introduced into the place of the organic constituents separated, it would not be difficult to account for the increased firmness and density presented by wood which has remained for some time under water.

It has been seen that the conversion of ligneous fibre into a pulverulent substance, and into humus, admits of adequate explanation by means of the three cases mentioned above, and what is especially important, that it may be supposed to take place independently of external oxygen. If this change takes place, as is described in III, the conversion of oak wood into the substance A shows that the carbonic acid disengaged amounts to only  $\frac{1}{3}$  as much as the water, while in the formation of the substances B and C none at all is disengaged. The formation of carbonic acid is then, during the first stages of the decomposition, either extremely small or altogether wanting. The change commences with the separation of oxygen and hydrogen in the form of water, and the separation of oxygen and carbon, as carbonic acid does not commence until a later period. It is likewise probable, that at a still later period carbon and hydrogen are separated in the form of carburetted hydrogen.

In the conversion of ligneous fibre into coal, these three cases may then be regarded as possible. In the first case the largest quantity of carbonic acid is formed, in the third the smallest; and also the former is attended with the greatest loss of volatile

constituents, and the latter with the smallest. If the change consisted solely in the separation of carbonic acid and carburetted hydrogen, only 22 or 25 per cent. of coal would have been formed; and as the specific gravity of coal is much greater than that of wood, the volume of the vegetable detritus lying at the bottom of the sea would consequently have diminished in a still greater proportion than its mass. Considerable depressions would thus have been caused during the formation of coal seams. But the conversion of ligneous fibre into the pulverulent substance and into humus, shows that the change commences with a separation of water, and that the third case occurs most frequently. Then, however, the loss of volatile constituents is far less, amounting only to about 50 per cent.

The values of  $x$  in the mean composition of coal, deduced from 49 analyses, are always rather more than in the mean composition deduced from the 67 analyses; still the greatest difference does not amount to more than 0.74 per cent. In the coals from the Marennen, however, it rises to 3.5 per cent. The values of  $y$  for the mean composition deduced from 49 analyses rise to 0.15 per cent. more than those for the coals of the Marennen. This shows very clearly, that the older the coal is the more complete the separation of oxygen and hydrogen. This is still more distinctly observable in the conversion of ligneous fibre into anthracite.

The same three cases may likewise be regarded as possible in the conversion of ligneous fibre into lignite. Assuming that the third only really occurs, which is undoubtedly the most probable of all, there is a loss of only 36 per cent. of the original substance. In the formation of fossil wood this loss decreases to 16 per cent., and the values of  $x$  and  $y$  amount to only about  $\frac{1}{5}$  and  $\frac{1}{2}$  of the same quantities in the formation of coal. These several amounts of loss and values of  $x$  and  $y$ , approximate to what we have already found them in the conversion of ligneous fibre into the pulverulent substance and humus. Consequently the change is not much further advanced in fossil wood than in these two substances. If, as is so frequently the case, this fossil wood is compressed by the weight of the overlying strata, we can understand why it may have a greater density than unaltered wood, notwithstanding this loss.

The value of  $x$ , in lignite, case III, is only 1.54 per cent. less, and that of  $y$  only 0.38 per cent. less, than the corresponding values in the mean composition of coal. If the conversion of



ligneous fibre into lignite resembles in general features its conversion into coal, it then follows that oxygen and hydrogen are separated in a far greater proportion during the first stages of change than during the latter. This is likewise in accordance with the fact already pointed out, that the values of  $x$  and  $y$  are but very little less for the coals of the more recent, than they are for those of the more ancient formations. During the enormously long periods, therefore, which elapsed between the formation of the more ancient coal and that of the lias coal, the former experienced but an extremely slight loss of substance. The conjecture that during the latter stages of the formation of coal, carburetted hydrogen is disengaged more copiously than any other product of the decomposition, gains great additional probability from the fact that a much more considerable quantity of this gas is met with in the coal beds of Lippe-Schaumburg than in those which belong to a more remote period (p.256), while it is wanting, as it appears, in beds of brown-coal.

Schrötter found that the residue left, after thoroughly extracting the brown-coal of Oberhart (XXVII) by means of ether, possessed very nearly the same composition as ligneous fibre.\* It follows, therefore, that the wood from which this brown-coal had been formed was altered only partially, and not in its entire mass. It would be very interesting to ascertain, by a similar treatment of other specimens of brown-coal, whether this is generally the case. The investigations which have already been carried out prove that numerous compounds of carbon co-exist in brown-coal.

The turf of Princetown gives greater values for  $x$  and  $y$ , and a greater loss of volatile constituents, than the fossil wood, and is consequently in a more advanced stage of decomposition. The values of  $x$  and  $y$ , and the loss of constituents for peat coal, approximate very closely to those for coal, especially that from the Marennen. It may, therefore, be inferred that this peat coal was actually passing into true coal, a change which since peat is a much more recent formation than brown-coal would favour the otherwise probable view, that the more delicate vegetable structures from which peat has been formed, are converted into coal more rapidly than thick trunks of trees. It is even probable that such trunks are never perfectly converted into coal.

\* This fact accounts for the very considerable quantity of acetic acid which was obtained on submitting this brown-coal to dry distillation. The wood contained in this coal was recognized to be coniferous.

It appears, and is also quite intelligible, that in the formation of fossil resinous substances rich in hydrogen, lignite passing into mineral resin, amber, retinite, asphalt, &c., the loss of constituents must be very considerable, assuming the change to be such as is described in the above-mentioned third case. It is, indeed, greater in the formation of the three latter substances than in that of coal. The values of  $x$  for these substances are much greater, and those of  $y$  much smaller; their formation consisting in the separation of large quantities of carbonic acid and very small quantities of water, while that of coal was precisely the reverse. These remarks will suffice to show that the most dissimilar substances may be produced from ligneous fibre, according to the nature of the change.

Among these resinous substances, amber demands our first attention, on account of its greater frequency. It occurs generally mixed with fragments of brown-coal, in all the countries surrounding the Baltic; more frequently, however, towards the south than the north, and not merely on the coast, where it is washed up from the bottom of the sea, but likewise inland. Bock states, that there is scarcely a village in East or West Prussia where amber has not been found in the fields. It has also been frequently met with in Lithuania, Poland, Silesia, Mark-Brandenburg, Lusace, Mecklenburg, Holstein, and Saxony. It is found in all the strata of the more recent diluvium and alluvium to a depth of 140 feet below, and in Pomerania to a height of 200 or 300 feet above, the level of the sea. Tracing the localities where it is collected, it is found that they converge towards one spot, which Berendt assumes to be in  $55^{\circ}$  north latitude and  $37^{\circ}$  to  $38^{\circ}$  longitude, in the basin of the Baltic. It has, moreover, been found in the neighbourhood of Gmünden, Ischl, and St. Pölten, in Austria, in France, Spain, Switzerland, Upper Italy, Sicily, upon Libanon, and the shores of the Caspian Sea, in Siberia, Kamschatka, Greenland, India, China, Madagascar, and North America.\*

Although there can be no doubt as to the possibility of ligneous fibre being converted into amber, still the insects and plants embedded in it, without having sustained any injury even in their most delicate parts, prove that it must have flowed from the stems and branches of trees, in the same way that resin is observed to flow at the present day. Moreover, the occurrence of amber between the an-

\* It is, however, doubtful whether the statements of travellers always refer to amber, and not to other fossil resins.

nular rings of carbonized trees, as well as the impressions of vegetable fibres in plates of this substance, afford evidence of such an origin. On the other hand, its occurrence disseminated throughout pitch coal, and alternating with beds of bituminous wood, as well as the fragments of brown-coal and the bituminous earth associated with it, countenance the assumption that it has been formed from ligneous fibre, more especially as the pieces of wood found with the amber do not generally belong to the amber trees, and as this wood is never found with it in large pieces or entire trunks.\* If it were merely an educt, the amber tree must have been as widely distributed in different climates as the amber itself. It may be, perhaps, that the progressive decomposition of brown-coal in sea-water containing but a small quantity of salt, especially favours the conversion of vegetable remains into amber; for the most extensive deposits of amber known are situated in the basin of the Baltic.

Retinite and asphalte, both so closely resembling amber, distinctly show that fossil resins may be formed by the decomposition of such remains. It is, therefore, very probable that amber is partly an educt and partly a product. Indeed, its varying colour, its greater or less transparency and capability of being decomposed, would appear to indicate that such is the case. It is worthy of notice that the amber recently thrown up on the sea-shores presents scarcely any decomposed crust, while in that which is dug out of the ground, this crust is from 1 to  $1\frac{1}{2}$  line thick, and sometimes even the entire mass has been converted into a crumbling substance.

Retinite occurs much less frequently in brown-coal than amber. It forms rounded fragments, from the size of peas to masses of 6 or 7 inches diameter, surrounded by an uneven dirty grey crust. It leaves but little ash when burnt. Ether and alcohol extract resins which are very similar. The composition of hartin from the brown-coal of Oberhart is, according to Schrötter, similar to that of retinite. The mineral resins examined by Johnston† and Henry‡ likewise resemble retinite.

The following analyses of different kinds of bitumen are given by Ebelmen :—

\* Unger, loc. cit., p. 151, et seq. Schrötter (loc. cit.) regards the resin dissolved out of amber by ether as the original vegetable resin, and considers it not improbable that the alteration suffered by this resin consisted merely in the conversion of a part of it into amber-bitumen. It corresponds in composition with mastic.

† Phil. Mag. 1838, March and July.

‡ Journ. de Chim. Med. 1825.

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Asb.
I. Bastennes ....	85.74	9.58	2.88	1.80	8.45
II. Pontnavey ....	67.43	7.22	23.98	1.37	15.83
III. Pont du Chateau ....	77.52	9.58	10.53	2.37	1.80
IV. From the neighbourhood of Naples ....	81.83	8.28	8.83	1.06	5.13

The analyses suffice to show that the composition of bitumen varies considerably. I approximates very closely to the coal containing the smallest per-centage of oxygen, but its hydrogen exceeds the maximum quantity contained in coal by about 2.4 per cent. II greatly resembles in composition the brown-coal, with the largest per-centage of hydrogen. III has very nearly the same composition as amber; and IV, that of asphalte. Therefore the most different processes of decomposition of organic substances may afford products which differ but little in their composition. The close correspondence between amber and the bitumen III, is another fact in favour of the former being a product of decomposition.

Asphalte is not an uncommon product of the decomposition of organic remains; it occurs in the more recent sedimentary formations, sometimes in large beds. According to Webster,\* there is in the island of Trinidad a bed of this substance a mile in length, and surrounded by an extremely luxuriant growth of plants resembling ferns.†

\* Edinb. New Phil. Journal. Vol. 18, p. 331.

† It has long been a prevalent opinion that the Dead Sea furnishes large quantities of asphalte. However, the researches of Robinson and Smith (Reports of the Association of American Geologists, &c., Boston, 1843, p. 371) render it probable that, whatever may have been the case in ancient times, it is rather a rare occurrence to meet with this substance in a large quantity in modern days, although small fragments may be occasionally picked up along the shore. Smith's perfect knowledge of Arabic gave him great facilities for obtaining information from the people. The Arabs told him that it was only after an earthquake that large masses of bitumen were found floating on the water. After the earthquake of 1834 a large quantity drifted ashore, near the south end of the sea, and six thousand pounds of it were brought to market by the Arabs. A mass like an island rose to the surface after the earthquake of 1837, three thousand dollars worth of which was sold. These are the only instances which were known to the Sheikh of Tehâlin, resident near the sea, a man fifty years of age; nor did his fathers hand down to him any tradition of other masses having been found. There is, indeed, a prevailing belief among the Arabs that the asphalte exudes from the rocks on the eastern shore of the sea, but there is good reason to doubt whether such is the fact.

If the asphalte comes to the surface of the Dead Sea after earthquakes, we must suppose it to be deposited in beds at the bottom, and loosened by the concussion. Its specific gravity is between 1.07 and 1.16; that of the water in the Dead Sea is 1.19, which, of course, accounts for its floating.



In the decomposition of vegetable substances there are formed, besides carburetted hydrogen, liquid and solid hydro-carbons, such as naphtha and petroleum or mineral oil, mineral tar, elaterite, naphthalite, ozokerite, &c.

Naphtha occurs at many places, especially in Asia, on the northern shores of the Caspian, near Baku, where it flows from a bed of clay marl, and is collected in wells dug 30 feet deep in the ground. In the Birman Empire there are more than 500 such wells in a small district near Rainanghong. The soil there consists of a sandy clay, covering a thick bed of slate clay, saturated with naphtha, under which is coal. At Colebrook-dale there is a naphtha spring rising from a coal seam. It likewise occurs at Amiano, in Parma, at Modena and Piacenza, near the Tegernsee in Bavaria, &c. The calcespar in the drusy cavities of alum-slate frequently contain an oil resembling naphtha, and recognizable by the smell when the mineral is rubbed or powdered. It would appear to be a product of the vegetable remains from which the combustible substance of the alum-slate has originated.

Since petroleum contains paraffine, a product of the dry distillation of vegetable substances, it was inferred that this substance originated from the action of subterranean heat upon coal. According to our knowledge of the increase of temperature towards the interior of the earth, coal-beds at a depth of about 8000 feet would possess a temperature of  $212^{\circ}$ ; and we may suppose that petroleum was distilled from such beds, and condensed at higher points. But in this case the temperature of the soil impregnated by it in places where it occurs in large quantities, as in Asia, must long since have been raised to a nearly equal degree, which is, according to the observations made by Abich (p. 252), by no means the case.

Mineral tar occurs in Persia, France, and several other places. That of Bechelbronn, in Alsace, occurs in a bed of freshwater sandstone. Elaterite is a rare product of the decomposition of vegetable substances; it is found in the coal-formation at Montrelais, in France, and at South Bury, Massachusetts. Hatchetin or schererite is likewise very rare. Near Merthyr Tydvil, in England, it is found filling small dykes, surrounded by calcespar, in the iron ores of the coal formation. At Loch Tyne, in Scotland, it floats upon the water in a peat bog. At St. Gallen, in Switzerland, it is found impregnating brown-coal and fossil wood. In the transition limestone of Beaulieu, in France, it occurs together with calcespar in druses. It occurs in Idria, together with cinnabar. The

ozokerite, which occurs in large masses at Slanik, in Moldavia, is likewise a variety of hatchetin.

The fichtelite found upon the stems of fir-trees in a bed of peat at Redwitz, the hartite upon the stems from the brown-coal of Oberhart, the koenlite from Utnach, and the tekoretin in the fir-trees from the bogs of Holtegaard, are all analagous hydro-carbons.

Wherever such hydro-carbons are found accompanying coal, and especially brown-coal, we may assume that the decomposition of the vegetable remains was such as is represented in the case I (p. 275). If, like petroleum, the mineral tar of Bechelbronn, elaterite, idrialine, hartite, tekoretin, fichtelite, and koenlite, they are richer in carbon than carburetted hydrogen is, a much larger quantity of carbon would be abstracted from the original wood during their formation than there was of carburetted hydrogen disengaged. If, like scheererite, they have the same per-centage composition as carburetted hydrogen, the decomposition may have been the same, with the exception that the carbon and hydrogen did not escape in the gaseous form of combination, but were separated as solid or liquid compounds.

Mellitic acid is a product of the decomposition of vegetable remains, differing from carbonic acid in the same way that the above-mentioned hydro-carbons differ from carburetted hydrogen, with the exception of scheererite. However, its extreme rarity proves that it was not formed so abundantly as the hydro-carbons, and that its formation was the result of altogether peculiar conditions. This substance occurs as a constituent of mellitite only in the brown-coal of Artern, in Thuringia, and Luschitz, in Bohemia, as well as in the coal of the lower green-sand, at Walchow, in Moravia. The same remarks apply to the oxalic acid contained in oxalite, which occurs in brown-coal at some few places.

The above investigations lead us to a probable view respecting the origin of the carbonic acid exhalations (p. 236). When the conversion of ligneous fibre into coal takes place, as in the case III, pure carbonic acid is disengaged without any admixture of carburetted hydrogen. We may thus account for the carbonic acid exhaled from more recent sedimentary formations, because it is possible that coal strata are buried beneath them. It may be that in the analyses of these exhalations such minute quantities of carburetted hydrogen may have been overlooked, as would result from the formation of anthracite (p. 278).

The brown-coal, in the form of bituminous wood, which occurs at Pützchen, on the right bank of the Rhine, opposite Bonn,

absorbs oxygen without disengaging carbonic acid. Upon corking up in a bottle some pieces of this bituminous wood, 11 per cent. of oxygen was absorbed during eight days. Further investigations must determine whether or not bituminous wood acts in the same way as ordinary wood charcoal, which absorbs continuously oxygen, forming carbonic acid and retaining it absorbed. Perhaps the oxygen absorbed by bituminous wood forms water with its hydrogen. This absorption accounts for the not unfrequent presence of foul air in brown-coal mines.\*

The bituminous wood, when exposed to the air, is converted in a short time into the finest pitch-coal, with a perfect conchoidal fracture and its peculiar fatty lustre.† Such a rapid change of form in vegetable remains, and such a perfect disappearance of the ligneous structure, is a very remarkable phenomenon, as the chemical changes go on so very slowly. It deserves further investigation, being calculated to throw much light upon the still obscure conditions under which the formation of coal and brown-coal has taken place.

The question must be raised as to whether a complete breaking up of vegetable substances is possible, *i.e.*, a complete conversion

\* R. F. Marchand (Journ. für prakt. Chem., Vol. 49, p. 467) examined the composition of the air in the brown-coal mine of Zscherben, at Halle. He found in the air at the entrance of the gallery 20·919 per cent. of oxygen, and 300 yards farther in, 20·521. From this point the proportion of oxygen steadily diminished, and in one place, where the lamps ceased to burn, it amounted to only 15·23 per cent. Neither carbonic oxide nor carburetted hydrogen could be detected. According to Marchand, it is the iron pyrites in the brown-coal which causes the absorption of the oxygen.

It is not to be denied that this substance has a share in the absorption: from my researches, however, it would appear that brown-coal itself has the power of absorbing oxygen to a very great extent. That very little or none of this gas goes to the formation of carbonic acid, is shown by the fact that the latter amounted, in the specimens of air examined, to only 0·22 per cent., corresponding exactly with the researches made by myself. Whether, in the pits of Zscherben, conversion into pitch-coal, or something similar, takes place, I know not.

† This change is essentially determined by the drying of the bituminous wood, for if it is placed under the receiver of an air-pump with oil of vitriol, the conversion is effected much more rapidly than in the air. The pieces enclosed in the corked bottle, where they could not dry, did not change in the least. The change, when going on in dry air, appears then to be caused jointly by the drying and absorption of oxygen, for a few pieces lying in a warm room for eleven days were converted into pitch-coal more completely than when under the air-pump. This bituminous wood cannot dry in its natural position; it lies beneath a bed of clay, which prevents the access of air. The perfect pitch-coal which occurs in many brown-coal beds, as at Meissner, in Hesse, may, therefore, have been exposed to circumstances which admitted of their drying.

The entire quantity of brown-coal taken from the above-named mine does not suffer this change, but only about a third part. In some parts of this coal bed it has never been noticed. The bituminous wood which passes into pitch-coal when exposed to the air, moreover, does not differ, when in a moist state, from any other kind of bituminous wood which does not suffer this change.

into binary compounds of their elements. The first and most rapid change which vegetable substances suffer when exposed to the action of water consists in the loss of their soluble constituents. These substances dissolved in water are in the most favourable circumstances for decomposition, especially nitrogenous substances are likewise present in solution, as in various kinds of fermentation. The residue remaining after the extraction of soluble substances by water—the ligneous fibre—is, in regard to the formation of both kinds of coal, of the principal importance. Even if all the oxygen is evolved in combination with carbon, there still remains a considerable quantity of the latter. This residual carbon can perhaps only be oxidized by free oxygen, which, however, has but very limited access to it, when the coal lies under the sea, or after the elevation of the strata, is buried between masses of rock. Still experience shows that coal, whether it has been formed by ordinary carbonization of wood, or by the action of water, is one of the most indestructible of known substances. About ninety years since, pointed piles were found in the Thames, at the place where, according to Tacitus, the ancient Britons had driven in a great number of such piles, in order to hinder the passage of the river by Julius Cæsar and his army.\* They were all carbonized to a considerable depth, had preserved their form perfectly, and were so hard in the interior that knife-blades could be made of them. As there is no chemical analysis of these piles, it cannot be decided whether they were merely carbonized, or more or less petrified. If the vegetable remains under water, or buried between rocks, were capable of being completely destroyed, we should not anywhere meet with coal, the age of which must be calculated by millions instead of thousands of years.

Nevertheless we see that, under certain circumstances, the ligneous fibre disappears, either completely or with the exception of very unimportant remains. The petrified wood is an instance of this, being nothing more or less than substitutions of inorganic substances for the original organic matter of the tissues.

When, moreover, we find that the least soluble inorganic substances, such as sulphate of baryta, &c., are displaced by other minerals, we must regard it as possible that even the ligneous fibre, or the carbon resulting from its decomposition, may likewise be displaced. However, I shall subsequently bring forward reasons for considering that the ligneous tissue of petrified wood has not been removed by a simple displacement, but by a process of decomposition.

\* *Chemisches Wörterbuch*, by Klaproth and Wolff. Vol. 3, p. 269.



During the formation of the carboniferous beds, all the rivers whose banks were covered with wood carried immense masses of driftwood down into the sea, as the large American rivers do at the present time which are flowing through wide tracts of uncultivated land. The culture of land has rendered circumstances entirely different. The banks of rivers have become arable and meadow land, while the woods have been destroyed for some distance from the banks. On this account the quantity of driftwood carried down by rivers flowing through cultivated land has become much less than that which they conveyed to the sea in præ-historic ages. Not only were trees and shrubs torn up by the roots by floods, but also the decaying remains of plants were swept into the stream, and carried into the sea. Every small brook and stream, overcharged after long rain or the melting of the snows, were laden with these substances. At that period, when the greater part of the earth's surface was covered with luxuriant vegetation, these waters carried almost only decaying vegetable matter along with them; while, at the present, they carry down far more inorganic matter, derived from cultivated land, than organic matter, the quantity of which is small since the crops are collected. Organic matter is, however, found upon analysing the suspended matter of rivers; in that of the Rhine it amounts to 3·31 (p. 123), and in the mud of the Nile to as much as 5·5 per cent. (p. 133).

From the same point of view Leopold V. Buch\* regards brown-coal beds as having been formed by brooks and streams carrying the leaves and trunks of trees from the woods upon the higher lands down into basins, lakes, and bays, where they were deposited together with mud.

The trunks of trees float in water, but if they retain their roots, which are often loaded with earth and stones, they readily sink, especially when soaked through with water. The trunks of trees, such as form the driftwood of the Mackenzie river, in the Stave Lake,† suffer a gradual decay, until they are converted into a blackish brown substance resembling peat; and layers of this often alternate with layers of sand and clay, the whole being penetrated by the long fibrous roots of willows, which grow on their trunks as soon as they appear above water. A deposition of this kind would produce, says Lyell, an excellent imitation of coal, with impressions of the willow roots. The banks of the Mackenzie present almost everywhere horizontal beds of wood-coal, alterna-

\* Lagerung der Braunkohlen in Europa. Berlin, 1851.

† Dr. Richardson, in Lyell's Principles, p. 716.

ting with bituminous clay, gravel, sand, and friable sandstone; sections, in short, of such deposits as are now evidently forming at the bottom of the lakes which it traverses. This wood-coal, after having been converted into this blackish brown substance, cannot fail to be rubbed off and carried into the sea during high water. A very great mass of driftwood is found where the Mackenzie reaches the sea.

When stems of trees are converted into fine powder, by decay or mechanical means, it sinks in still water. This is the case not only with heavy woods, as oak, beech, and pine, but also with willow wood. It is only imperfectly decayed ligneous fibre which floats. Decayed spongy beech-wood, sometimes quite bleached, and in which the inside wood is often altered, sinks when rubbed to powder; not, however, till after some days, if it be in large pieces. Some dark-brown pulverulent ligneous fibre, resulting from the decay of heath plants, which I found in a forest, washed into the road by a heavy rain, sank immediately in water. Oak, fir, and poplar sawdust likewise sink, but splinters float in water. Even finely powdered dead leaves sink. The particles of wood, whether decayed or mechanically divided, also sink in seawater. There is no doubt that it is merely necessary to displace the air in wood by water in order to cause its sinking.

In the moving water of rivers, finely divided, decaying vegetable substances are not deposited, or at most, only temporarily; they are therefore carried into the sea or lakes, and sink in still water. This is also the case with the same kind of substances swept into the sea by the waves dashing upon the shore, and by the tides.

Although these organic substances are but little denser than water, while the inorganic matter suspended in river waters is  $2\frac{1}{2}$  or 3 times as dense as water, the former sink much sooner than the latter. Muddy Rhine water does not become clear until after it has stood four months (p. 123 note). If, therefore, decayed vegetable matter, and finely divided inorganic matter, are simultaneously carried into the sea, very little of the latter sinks with the former. For this reason, the inorganic matter of coal always amounts to much less than the carbonaceous, as is evident from the analyses of coal and brown-coal.

It is easy to imagine that in præ-historic ages, the quantity of decayed vegetable substances (vegetable detritus) carried into the rivers must have amounted to much more than that of the trees actually carried into them as such; for only the trees torn up from

the banks and steep declivities of the rivers came into them in a perfect state, and not those which died upon the high lands and slight declivities. It was not until after these were decayed, that they could be carried away by water. Then the area of the high plains and the slightly inclined land is, when the rivers flow through narrow valleys, far greater than that of the overflowed banks and the steep declivities. The dead trees upon slight inclinations are more or less fixed to the ground by their roots, and, like blocks of stone in the same position, are not carried away by the streams until after they have suffered decomposition.

No one doubts that the rocks constituting continents and islands have furnished the material for the formation of sedimentary deposits in the sea, and still continue to do so. Large masses of rocks must have been mechanically and chemically broken up, in order that a sufficiency of suspended matter might be carried into the sea for the formation of the thick beds associated with the coal seams. Long periods of time were necessary for this, during which the vegetation was again and again destroyed. If the strata of the coal-formation were derived chiefly from transition rocks, we should find upon them the rich remains of many destroyed vegetable worlds, if they had not been carried away. But we find, in the frequently unfruitful earth upon these rocks, only scanty remains of those past vegetations. Does not the idea suggest itself, that these remains, which we find in such large quantity between the sedimentary strata of the coal basins immediately following the transition rocks, are the very remains which we in vain seek for upon the elevated plains and the declivities of mountains?

If the vegetable remains had, during a long series of years, accumulated to such an extent upon the earth's surface, that even the longest roots of the trees could no longer reach to the soil beneath, the consequent deficiency of requisite inorganic substances would have restricted their growth. The rain-water, which at the present time readily extracts these substances from the vegetable mould, conveying them in solution to the roots of plants, would only have been able to take up the scanty quantities which were retained in dead plants. There would finally be a total deficiency of these inorganic substances, and vegetation would have ceased altogether. Springs and rivers would then alone have contained these substances in a state of solution, and that ground only which was overflowed by their waters could have received a supply of them. Consequently, vegetation would still have continued in the valleys, where the quantity of vegetable remains would have con-

tinually increased, but not upon the elevated plains, which were wanting in a supply of water from springs and rivers.

But this was not the case, and could not have been; for fertile soil was carried down by the rivers from the mountains and their declivities to the valleys, as at the present time. The quantity of vegetable matter in the detritus must have been far greater in proportion to the inorganic matter than now in cultivated countries; for at that period, all the plants which are now harvested, all the wood which is burnt, underwent decay. Nor were there any bare fields, from which such large quantities of inorganic matter are now carried into the rivers.

Let us imagine the hydrographical basin of a large river during the præ-historic age.\* It is easy to calculate how much vegetable matter was annually carried to the sea, and that the remains of one year's growth would be sufficient for the formation of a thick coal-seam, if they were spread over a portion of the sea's bottom equal in area to about one-thousandth of the river basin. But if we venture to remember, that the forest trees require a period of centuries to attain their full growth, we shall understand that the annual produce of vegetation accumulating after dying for such a long time, would soon yield a quantity of vegetable matter a hundred times as great as the annual production. A single season would then be sufficient, if there were much rain or snow, to carry down a large quantity of this long accumulating vegetable matter into the sea, furnishing the material for very large coal-seams.†

\* I do not forget that at the coal period, the continents were less extensive than at present; and that, consequently, the large basins of modern rivers cannot be taken as a standard for those which then existed.

† Geologists have found very great difficulties attending the supposition that the vegetables have been swept by strong currents of water into the position where we now find them; for not only have similar effects been produced over considerable areas, but the vegetables have suffered very little injury, their delicate leaves being most beautifully preserved. Now, though we know that vegetables are abundantly borne down by river floods into the sea, they by no means remain uninjured; and if they be of a soft nature, such as the bulk of the coal plants are considered to have been, the damage done them by transport is considerable, as De la Beche had occasion to remark on the coast of Jamaica, where arborescent ferns and other tropical productions are sometimes, though very rarely, carried by floods from the neighbouring mountains into the sea. In the few instances which came under his observation, the fern trees were so damaged in the river courses, as to be with difficulty recognized.—Geological Manual, p. 427.

A wider distinction must be drawn between the compact masses of coal in which scarcely any or no vegetable remains are recognisable, and those in which they are distinctly preserved. The former were formed from vegetable detritus, and for this reason it is very probable that the plants from which they were formed had been carried a long distance by rivers, while, on the contrary, the plants, whose remains are well preserved, grew upon the sea-shores, or upon low islands. But how is it possible to suppose, that the amorphous coal had been formed from



The rapidity with which decayed and finely divided vegetable remains sink, compared with the suspended mineral matter, in water, shows that the one might be deposited without any very great admixture of the other. There may even have been a separation of the larger remains from the decayed and disintegrated substances, for these sink immediately, while the former remain some time floating.

The mechanical structure of coal, its inorganic constituents, the character of the strata in immediate contact with the coal-seams, all afford evidence in favour of the sedimentary formation of coal upon the bottom of the ancient seas. We are indebted to several geologists for valuable observations and researches on this subject. Those by Henry Rogers,\* on the Appalachian coal-bed in the United States are especially important, it being by far the most extensive yet explored in any country. A comparison of the carboniferous strata of contiguous basins has convinced him that they are only detached parts of a once continuous deposit, and the physical structure of the whole region most satisfactorily confirms this idea, by showing that they all repose conformably on the same rocks. Upon a moderate estimate, the superficial area of this great basin amounts to sixty-three thousand square miles. I would ask, says Rogers, is it conceivable that any lake, bay, or estuary, could have been the receptacle of a deposit so extended, or that any river or rivers could have possessed a delta so vast?

With regard to the mechanical structure of the Appalachian coal, Rogers remarks, that "each bed is made up of innumerable very thin laminæ of glossy coal, alternating with equally minute plates of impure coal, containing a small admixture of finely divided earthy matter. These subdivisions, differing in their lustre and feature, are frequently of excessive thinness, the less brilliant leaves sometimes not exceeding the thickness of a sheet of paper. In many of the purer coal-beds, these thin partings between the more lustrous layers, consist of little laminæ of pure fibrous charcoal, in which we may discover the peculiar texture of the leaves, fronds, and even the bark of the plants which supplied a part of the vegetable matter of the bed. All these ultimate divisions of a

the same material which composes these fossiliferous beds, even when they are in immediate contact! Do not well-preserved remains of marine animals occur in strata, the material for which was brought from great distances by rivers? We find the most distinct impressions of plants in the strata alternating with the coal-seams. In this case, it is unmistakable that the plants growing quite near to the sea, have been deposited simultaneously with the suspended earthy matter.

\* Loc. cit.

mass of coal will be found to extend over a surprisingly large surface, when we consider their minute thickness. Pursuing any given brilliant layer, whose thickness may not exceed the fourth part of an inch, we may observe it to extend over a superficial space which is wholly incompatible with the idea that it can have been derived from the flattened trunk or limb of any arborescent plant, however compressible. When a large block of coal is thus minutely and carefully dissected, it very seldom, if ever, gives the slightest evidence of having been produced from the more solid parts of trees, though it may abound in fragments of their fronds and deciduous extremities."

This description is quite in accordance with the opinion that, besides the large quantities of decayed vegetable remains, which, in their conversion into coal, lost what slight traces of vegetable structure they still retained, others were deposited here and there, whose forms were better preserved. The minute plates of impure coal prove that the finely divided earthy matter did not in all cases remain suspended.

I agree with Rogers in the opinion, that it is difficult to understand why the coal should not consist principally of the larger parts of trees, such as their trunks, limbs, and roots, if any species of drifting operation brought together the materials of the bed, by conveying seawards the growth of ancient forests. It is, however, necessary to limit it so far, that although it is certainly more difficult to conceive the conversion of trunks of trees, as such, into coal, still it is not improbable that this might have taken place, had they previously passed into the state of the blackish brown substance constituting the mass of the trees floated down by the Mackenzie river (p. 295).

"The lowest member of the Appalachian coal-formation is a thick bed of uncommonly pure coal; the middle a layer of soft shale or fire-clay, about one foot in thickness; and the uppermost or roof coal, is itself a compound seam, two or three feet thick, of alternating layers of coal and fire-clay. Now it is a highly instructive fact, that this general triple subdivision prevails throughout nearly the whole range of the seam, from its eastern to its western outcrops. Such a fact is, however, conclusive as to the uniformity of the conditions under which every part of this coal-bed was produced."

"In many of the purest layers of these coal strata, the total proportion by weight of foreign mineral substance in the coal is less than 2%, sometimes barely 1%. "This agrees perfectly with

the facts of the rapid deposition of finely divided decayed vegetable substances, and the slow deposition of mineral substances. Rogers considers such an extremely insignificant quantity as inconsistent with the notion of a drifting of the vegetable matter itself, which, according to any conceivable mode of transportation, would be accompanied by a large amount of earthy matter, such as abounds in all deltal deposits, and even mingles with the wood in the rafts of the Atchafalaya.\* It must, however, be observed, in opposition to this, that the vegetable detritus would be deposited, in any case, before the earthy, and the trunks of trees last of all. Each would, therefore, form separate layers. If, again, the earthy matter was in tolerably coarse particles, it would be the first to sink."

The floor upon which each seam of coal in the Appalachian coal-beds immediately rests, is, with a few rare exceptions, wholly distinct in composition from the roof, consisting of a peculiar variety of more or less sandy clay, distinguished by its containing the *Stigmaria fucoides*,† which, according to Rogers, is the plant to which we may chiefly ascribe the vast stores of fossil fuel.

In the Appalachian coal-formation the limestones, both pure and magnesian, containing a variety of marine organic remains, occasionally compose the floor or roof, sometimes in direct contact with the coal. In some spots the pure coal is not separated from the pure limestone by more than a single inch, and then the interval is filled with a calcareous carbonaceous shale. In other places a bed of fossiliferous limestone embraces a thin seam of coal, in almost direct contact.‡ Many of the thicker strata consist of alternating layers of limestone and soft shale.

Limestone is a chemical deposit formed under the influence of vital action. When free from argillaceous and siliceous matter, it

\* According to Lyell (*Principles*, p. 213), the Atchafalaya, an arm of the Mississippi, catches a large portion of the timber annually brought down from the north; and the drift trees, collected in about thirty-eight years previous to 1816, formed a continuous raft, no less than ten miles in length, 220 yards wide, and eight feet deep. This prodigious quantity of wood illustrated the manner in which abundance of vegetable matter becomes, in the ordinary course of nature, imbedded in submarine and estuary deposits. It is also found in excavating at New Orleans, even at a depth of several yards below the level of the sea, that the soil of the delta contains innumerable trunks of trees, layer above layer, some prostrate, as if drifted, others broken off near the bottom, but remaining still erect, and with their roots spreading out on all sides, as if in their natural position.

† Mr. Logan (*Proceedings of the Geological Society*, No. 69) has found that the floor of every coal-seam in South Wales is composed of the same material.

‡ Such a direct contact is also frequently found in European coal strata.

has been formed in water containing no suspended matter ; but its formation is not entirely stopped by the presence of suspended matter in sea-water, for some of the Appalachian limestones contain a considerable quantity of this matter. It appears, however, that their formation ceased when the quantity of suspended matter increased very greatly ; in this case only mechanical deposits took place, upon which pure chemical deposits were again formed as soon as the water became clear. The alternating layers of limestone and clay were formed in this way.

The mechanical deposits of vegetable detritus which had been suspended in the sea appear to bear the same relation to the chemical deposits as those originating from suspended earthy matter. While the former were being deposited, the chemical deposition of carbonate of lime was not wholly interrupted, for the ash of coal sometimes contains carbonate of lime (p. 266). Again, dark carbonaceous limestone occur between the coal-seams, which exhale a bituminous odour when rubbed. This limestone may have been formed by vegetable agency (p. 189).

The universal difference between the formation of chemical and mechanical deposits is, that the material for the former is always present in a state of solution, while the material for the latter is suspended in greater or less quantity, sometimes scarcely perceptible. If the quantity of this suspended matter is very minute, the chemical precipitates are entirely or almost free from mechanical admixtures. If, on the contrary, they are present in large quantity, they render the chemical deposits more or less impure. But the great similarity between the earthy constituents of coal and those of the shale strata associated with it (p. 269) show that both earthy and vegetable substances were suspended together in the water of the sea. When these substances sank together, the deposit was a proportionately impure coal ; and when they sank in natural succession, gave rise to pure coal and mineral strata ; we have, however, already seen (p. 296) that the periods of the deposition of the vegetable matter and that of the earthy matter may have been very far apart.

These views are strongly favoured by the important researches of Murchison, De Verneuil, and Keyserling.\* According to them, the sections of the coal works of Lissitchia Balka, and of the southern regions of Russia, assure us that the hypothesis of the formation of coal-beds from masses of vegetation, and that the ground upon which they grew had subsided *in situ* (the truth of

\* The Geology of Russia, 1845, vol. I. p. 113.



which, as regards some coal-basins, cannot be disputed), cannot be applied to the cases in question, any more than to pure marine coal-beds of the northern districts of Northumberland and the north-western parts of Yorkshire, &c. We meet with a confused assemblage of many terrestrial plants, both above and below the coal-seams at Lissitchia Balka, whilst from the uppermost to the lowest bed, throughout a thickness of about 800 feet, the shells are exclusively of *marine* origin. What, then, does the finely levigated shale or clunch, which is the support of the coal-seams, indicate but that in those periods when the bottom of the sea was spread over with the detritus of matted and broken plants, washed into it by inundations or freshes of former rivers, that the heavier earthy matters which accompanied such accumulations (in the same way as in the floating islands or snags of the great American rivers) sank to the bottom, whilst the lighter plants floated, and formed the upper stratum?

The plants thus left upon the muddy slime, which had either been drifted with them, or derived from the destruction of the lands on which they grew, were subsequently covered by other sediment, sometimes in the form of siliceous sand, at other times of argillaceous matter, impregnated by calcareous springs, thus accounting for the varied nature of the roofs of the coal-seams, which consist of grit, sandstone, or limestone, according to the condition of the water which succeeded the deposit of each layer of vegetable and earthy matter. We may, however, express our belief that here, as elsewhere, some of the coal which is found in strata alternating with marine deposits may have resulted from the washing away and entombing at short distances from their original site, of the low jungle edge of tropical islands; in other words, by the sinking into the adjacent seas of floating masses of matted earth and plants.

On the left bank of the embouchure of the Dwina, at Archangel, these geologists\* found "the cliff to be composed of the following materials in descending order:—1st, vegetable soil and boggy woodland; 2nd, clay and sand, alternating in fine laminæ with fragments of decayed wood, and indicating the deposit by the river; 3rd, bog and peat, the remains of a former decayed vegetation, with blackened and rotted roots, &c.; 4th, river sand repeated; 5th, stiff blue clay, reaching down to the water's edge. Now this arrangement seemed to the observers very distinctly to indicate the alternation of river freshes or inundations, with periods

\* Loc. cit. p. 570.

of dry land on which vegetation went on, while the blue clay or base of the section might represent the ancient bottom of the estuary. The overlying beds offer all the analogy which we require in order to account for the phenomena prevalent in some of our coal-fields, of the alternation of certain beds of coal and shale, wherein all the plants present the appearance of having been entombed *in situ* with other large layers, indicating the action of drift. For if this low left bank were submerged, and its materials consolidated by long-continued pressure, we might doubtless anticipate that there would be produced two distinct carbonaceous masses; one, in fact, formed from vegetation *in situ*, while the other, composed of estuary silt, and converted into carbonaceous sandstones and shale, would contain, here and there, fossil stems of trees which had been drifted by the stream and placed irregularly, either athwart the strata, or laid along them in flattened masses.”

The abundant resources of a vegetation extending over whole continents, and whose remains were brought to the sea from the most distant points by the rivers, appear to have been hitherto generally overlooked;\* the materials for the formation of coal were sought only in the limited vegetation of peat moors, upon low islands, and the low plains covered with dense tropical woods, and sunk beneath the sea. All the hypotheses referring to the formation of coal from partial vegetable remains, agree in ascribing the origin of coal to materials comparatively less abundant than is consistent with the immense quantities of this substance, while they afford no evidence of what has become of the vast masses of vegetable matter which in præ-historic ages covered the continents before the existence of herbivorous animals. I do not, indeed, forget that during the coal period there were only transition and crystalline rocks above the surface of the sea, and that the continents were far less extensive than at the present time; but it is precisely for this reason, that the remains of plants growing upon these lands, and even the unaltered plants themselves, could be more easily carried into the sea.

All vegetable substances which reached the bottom of the sea

\* That some of the trees which are found erect in the coal-formation, have not been drifted, is, as Buckland (Anniversary Address to the Geological Society, 1841) says, established on sufficient evidence; but there is equal evidence to show, that other trees, and leaves innumerable, which pervade the strata alternating with coal-seams, have been removed to considerable distances from the swamps, savannahs, and forests that gave them birth; particularly those which are dispersed throughout the sandstones or mixed with fishes in the shale-beds.

would, after all their soluble parts had been extracted, be converted into coal. This was likewise undoubtedly the case with plants growing upon the bottom of the sea, and the algæ floating in it. As they never occur at a depth of more than 200 feet, and only near the shores, and as the extensive accumulations of large species of fuci form impenetrable vegetable masses only on the shallow shores of the ocean, it is certain that these marine plants can only have given rise to the formation of coal seams which now lie at small depths below the earth's surface, unless a subsequent sinking of the strata has taken place. The floating algæ,—like those forming on the south of the Azores a collection of more than 4000 square miles, bounded by the Gulf Stream,—must, however, have sunk when they had become denser in consequence of decay, while the plants on the surface were continually renewed, and thus furnished abundant material for the formation of coal.

Unger,\* although doubting the possibility of such a formation of coal, because, without any exception, both coal and brown coal appear to be products of the decay of terrestrial plants, does not offer any explanation of the disappearance of the enormous masses of marine plants which have been produced since the first existence of the vegetation upon the earth. Fuci, exposed to the influence of a high temperature and water, are decomposed after a few days; therefore it cannot be doubted that after their decomposition they would have sunk in the sea, and furnished material for the formation of coal: moreover, varieties of fuci actually occur in a fossil state in coal.†

De Luc, A. Brongniart, E. de Beaumont, Macculloch, Göppert and others have put forward the view that coal has been formed from a kind of peaty deposit. More recently Unger‡ has endeavoured to prove that coal corresponds with turf in composition, structure, and stratification, and is therefore to be regarded as having a similar origin.

It cannot be doubted but that peat has furnished material for the formation of coal; the similarity in the composition of peat and coal, and especially brown coal (pp. 264, 265, and 287), proves this. But if the similarity of situation is to be admitted as evidence in favour of this view, it is presupposed that the conversion of peat into coal has taken place upon the spot. Admitting that by this mode a coal may have been produced, containing like those analysed by

\* Loc. cit. p. 105.

† Bronn, Handbuch einer Geschichte der Natur, T. III. p. 61.

‡ Loc. cit. p. 110, etc.

Kremers and Taylor, shale substance disseminated throughout, this circumstance can only be explained by assuming that the beds of peat have been sunk beneath water containing this substance in a state of suspension.

The ash of peat contains no alumina,\* and throughout the whole vegetable world it occurs only in extremely small quantities, consequently it must have been introduced mechanically into all kinds of coal where it is found. As this earth is never found as such in a state of suspension in water, but always in combination with silica, this substance would also have been mixed with the coal.

Some geologists, and especially E. de Beaumont, have assumed, in order to account for the frequent alternation of coal seams and sedimentary rocks with marine products, a continuous sinking of islands, so that each coal seam was covered with sediment up to the level of the sea, and a new flora afterwards grew there, which was in its turn sunk below the water, and so on.† This idea seems to be confirmed by the opinion of many botanists, who declare that the vegetation of the carboniferous period possesses the character of an insular flora, such as might be looked for in islands scattered through a wide ocean in a subtropical and humid climate.

The conversion of the vegetation upon islands into coal can only be imagined by supposing that the plants were so far decayed before being sunk, that they had become vegetable mould. But if this was not altogether the case; if at the time of the sinking there were, besides these decayed substances, stems of trees or larger remains of plants, which sunk with them, we ought to find these now, at least here and there. But the coal itself contains only a few traces of forest trees, either in a prostrate or erect position, while their broken stems are found mingled with fragments of stigmaria in more or less abundance in all the coarser rocks. When trees, or other parts of plants, come under water, they almost entirely lose their organic matter, and, at the same time, retain

\* Liebig, loc. cit. p. 324.

† H. Rogers (loc. cit. p. 464) supposes that the whole period of the coal measures was characterized by a general slow subsidence of the coasts on which, we conceive that the vegetation of the coal grew—that this vertical depression was, however, interrupted by pauses and gradual upward movements of less frequency and duration, and that these nearly statical conditions of the land alternated with great paroxysmal displacements of the level, caused by the mighty pulsations of earthquakes.

Although it cannot be denied that such movements have taken place on the crust of the earth, I do not consider it requisite to assume that they played this part in the formation of coal basins, for the reasons which I have already brought forward, and shall do subsequently.



their form, as is the case with fossil wood, &c. It cannot be assumed that the trees standing erect in peat bogs, and extending through all their strata, would have escaped such a change; for as the surrounding peat took up the earthy substances suspended in the sea during its conversion into coal, the stems of trees would have likewise done the same, and become petrified.

Rogers imagines that the areas now covered with the coal formation have possessed a physical geography of which the principal feature was the existence of extensive flats bordering a continent, and forming the shores of an ocean, or some vast bay, and that this low coast was fringed by great marshy tracts or peat bogs, on which along the landward margin grew the Coniferæ, tree ferns, Lycopodiaceæ, and other arborescent plants. Admitting this assumption, we arrive at the following conclusions. The products of the decay of meadows of stigmæria would have been, in the first instance, carried into the sea by tides and torrents. The vegetable parts of this matter would have sunk immediately, while the earthy parts remained, for the most part suspended if they consisted of such fine particles as shale and fine clay. So long as the washing away of the vegetable mould continued, the trees, which were fixed by their roots to soil below, would have remained standing. When ultimately these strata were attacked by the floods, the trees would have been washed into the sea. If these strata consisted of fine clay, they would have furnished material for the formation of shale; if on the contrary they consisted of coarser rocks, they would have given rise to the formation of sandstones or conglomerates.

If the roots of the trees swept into the sea were loaded with stones and other heavy matters, they would have sunk immediately with the coarser earthy particles, and formed the roof of the previously deposited finely divided vegetable remains. If these trunks of trees were free from heavy matter, they would have floated, and not sunk until after they had either been entirely saturated with water, or were so far decayed as to be heavier than water. In this case the coarser rocks would have been deposited directly upon the finely divided vegetable remains, and afterwards the trunks of trees \* upon them.

Such geognostic relations are met with in the Appalachian coal fields as well as in others. According to H. Rogers the roof of these coal strata consists oftentimes of very coarse rocks. In these

\* That the driftwood, in large quantities, is drifted about in all directions to very distant parts of the sea by currents, is manifest from many facts which Lyell (*Principles*, p. 717) quotes.

instances the inclosed vegetable remains are for the most part fragments of the larger stems or branches of gigantic arborescent plants, their fronds and leaves being less abundant. These fragments occur in all positions as regards the plane of the bedding,—horizontal, oblique, and perpendicular,—and betray, in their broken condition and irregular mode of dispersion, the sudden and tempestuous character of the currents which drifted and entombed them. A further indication of the violence of the currents which strewn these coarse materials over the coal, is sometimes to be detected in the composition of the lowest portion of the overlying bed of grit or sandstone, throughout which a large amount of coal is disseminated, in the state of powder or sand, giving the rock a dark speckled appearance. This is of very common occurrence in the anthracite coal strata of Pennsylvania, where the coarse grit not unfrequently rests immediately upon the coal. This implies, as Rogers imagines, the erosion of a certain portion of the upper surface of the soft carbonaceous mass, by the friction of the sandy current. The coaly matter, thus disturbed, would have subsided with the first layers of the sand with which it was mingled. He also alludes to Mr. Logan's communication of a still more striking proof of the energy of the movements which occasionally took place during the formation of the coal measures. This observer gives an account of actual boulders, or rounded pebbles of coal, in the Pennant grit, and other coarse strata of the coal field of South Wales. These facts prove incontestably the energy of the causes which washed away the coarse rocks and large arborescent plants from the shores of an ocean.

In the other case, when the soil upon which the trees grew consisted of fine clay, the results must have been different. The particles of this clay would have remained longer suspended in water before sinking. It might, therefore, happen that the stems sank before the argillaceous matter, and were deposited immediately upon the finely divided vegetable remains. Petrified stems of trees are actually found in the shale beds immediately above the coal seams. If the bed of vegetable mould upon the shore of the ocean was not very thick, large masses of the underlying clay must have been washed away by the tides before the roots of the trees were so far loosened that they could be carried away. Meanwhile the suspended earthy matter would have been deposited upon the already formed bed of finely divided vegetable matter, forming immense strata of shale, and the stems of trees which sunk afterwards would have been enclosed in the earthy matter con-

tinually being deposited. We may in this way account for the presence of petrified stems of trees in shale, which will be noticed further on.

The shale strata were formed as much from the mineral substances washed from the shores by tides, as from the suspended matter, conveyed into the ocean by rivers, from the interior of the country. If there was any difference between these substances in the size of their particles, different kinds of deposits would have been formed according as one or the other preponderated. The substances washed from the shores may have been larger grained and more siliceous than those carried down by the rivers, the degree of subdivision of the latter depending in great measure upon the distance they had to travel. The frequent alternation of strata, varying in texture, and rich in, or free from, quartz, may therefore be owing to differences in the origin of the suspended substances from which they were formed. The vegetable detritus accompanying both the earthly substances washed from the shores, and those carried down by rivers, mixed together, would likewise have furnished material for the formation of coal.

The grit and pebbles from which conglomerates are formed can evidently only have been transported upon the bottom of rivers and the sea by the currents and tides, and, therefore, may have originated partly at a distance from the sea-coasts, and partly near to them.

Conversion into coal is not the only change to which vegetable substances are subject. The substance of some organic bodies may be replaced by mineral matter, in the same way that one mineral is replaced by another. Petrification is a change of this nature. The petrification of a tree floating in the sea may be commenced by the substances dissolved in sea water, and if it advances so far that the specific gravity of the tree becomes greater than that of water, the tree sinks and the petrification is completed at the bottom of the sea.

On treating a *Stigmaria fucoides*, fossilized by carbonate of lime, from the transition formation, with diluted hydrochloric acid, Göppert\* obtained a residue presenting the entire structure of the plant in its natural arrangement and colour. The wood of coniferæ, from transition rocks, left only 0·02 to 0·07 of feebly brown, perfectly flexible fibres together with some empyreumatic oil smelling like creosote. On treating silicified wood with moderately strong hydro-fluoric acid, he obtained a ligneous residue, which for the

\* Jahrbuch für Mineralogie, &c. 1837. p. 370.

most part indicated the species of the wood. Such silicified wood is found in the coal formation (Lobejün near Halle, Neurode in Glatz, Radnitz in Bohemia).

If we endeavour to ascertain, by what substances contained in sea-water the organic matter of the petrified wood was so far decomposed that it could be removed, we cannot ascribe this change to any other than the sulphates. These salts are deoxidized by organic substances in the presence of water (chap. 1, No. 27), and thus the carbon and hydrogen of these substances undergo indirect oxidation, although the former resists the direct action of the oxygen absorbed by sea-water. These two bodies are separated in the form of carbonic acid and water. Such a deoxidation of sulphate of lime has been clearly proved to take place, although this has not yet been done with regard to sulphate of magnesia. The sulphate of lime in sea-water may, therefore, be regarded as the agent employed by nature for the entire removal of organic matter during the process of petrification.

Sulphuret of calcium is decomposed by carbonic acid. A stream of this gas, passed through a solution of the salt, gives rise to the formation of a precipitate of carbonate of lime, consequently these substances being both formed simultaneously in the deoxidation of sulphate of lime by organic matter, they would react upon each other, and the deposition of carbonate of lime in the place of the organic matter of the wood may thus be accounted for. According to Gay Lussac and Thénard, oak-wood contains 52.53 per cent. of carbon, which decomposes 295 parts of sulphate of lime, yielding 190 parts of carbonic acid, of which the half is employed in the decomposition of the sulphuret of calcium, yielding 217 parts of carbonate of lime, while the remainder escapes.\* According to this calculation 217 parts, by weight of carbonate of lime would be introduced in the place of 100 parts of wood; and as these numbers bear very nearly the same proportion to each other as the specific gravities of substances, the carbonate of lime would very nearly occupy the space left by the decomposed wood.

Göppert† gives a description of tuberous masses with branches, from the coal mines of Mark, in Westphalia, filled with iron pyrites, and occurring in the coal itself. They are frequently

\* The whole of the carbon and hydrogen cannot exercise a deoxidizing action, for wood contains hydrogen and oxygen in the proportion to form water. Therefore, the above calculation is founded upon the assumption, that only the carbon of the wood effects the decomposition of the sulphate of lime, and that the hydrogen and oxygen of wood escape in form of water.

† *Zeitschrift der deutschen geol. Gesellschaft.* Vol. iii., p. 291.



covered with a crust of very fat, smooth, and brilliant coal,  $\frac{1}{4}$  or  $\frac{1}{2}$  an inch thick, after removing which, the organic structure, the cicatrices of the stigmaria are visible, generally with the lustre of iron pyrites. The frequent occurrence of this mineral in coal, as a coating upon vegetable impressions in shale, &c., and as an incrustation upon fossil shells, shows that its formation at the cost of organic remains is a very frequent phenomenon. (Chapt. I., No. 28.) This formation of iron pyrites can only be explained by the presence of sulphates; and, so far as it goes on in the sea, only by the decomposition of sulphate of lime. The 52·53 parts of carbon in oak-wood yielding, by decomposition of sulphate of lime, 69 parts of sulphur, which would have given 127 parts of iron pyrites; consequently, only 25·4 parts by volume of this substance would have been introduced into the place of 100 parts by volume of wood. The remaining space might have been filled with carbonate of lime, formed by the decomposition of sulphuret of calcium by means of carbonic acid. But iron pyrites does not occur associated with carbonate of lime; and it is therefore difficult to account for the complete filling of vegetable remains by iron pyrites,\* if it may

\* It is not merely the sulphates conveyed to plants by water which contribute to the formation of iron pyrites, but also those which are found in their ashes. The ash of beech wood contains as much sulphuric acid and peroxide of iron as would suffice to form iron pyrites amounting to  $\frac{1}{48077}$  of the weight of the wood. The peroxide of iron would yield 23 times as much pyrites, if sulphates were brought in contact with it from outwards. Fir wood can give rise to the formation of ten times as much iron pyrites as beech wood. The fuci contain very large quantities of potash, soda, and lime, combined with sulphuric acid. According to Forchhammer, the average percentage of sulphuric acid in 19 varieties of fuci amounts to 3·82 per cent. of the dried plants. Girardin found 13 to 22 per cent. sulphate of potash in Varec salt, and 30 per cent. sulphate of soda in a specimen of soda from Alicante.

The large quantities of carbonic acid which the fuci during their decomposition afford, disengage sulphuretted hydrogen from the reduced sulphates. In the neighbourhood of Copenhagen, the evolution of this gas is so great, that the silver articles in the houses near the coast are constantly blackened. If the seaweeds, while in this state of decomposition, come in contact with peroxide of iron, pyrites are formed. At Kronberg, near Helsingör, such large quantities of seaweed are thrown upon the coast annually, that the sulphur they contain amounts to as much as that in 332,000 pounds of iron pyrites.

Durocher and Malguti (l'Institut. 1852, xx., p. 138) found in a blueish marl, which is continually being deposited at a little distance below the level of the sea upon the coast of St. Malo, 0·002 iron pyrites. It is not formed in deposits consisting entirely of sand, and it is very rarely met with in pure quartz sandstone, because it has a great tendency to combine with oxygen, and consequently can only exist in very impervious rocks. According to Ebelmen, the Jura limestones owe their blueish colour to the admixture of about 0·002 of iron pyrites. All these facts tend to show that the formation of iron pyrites in the sea is very general.

Ceramites occur frequently in the silurian alum schist of South Norway. Forchhammer does not doubt that its large quantity of carbon, sulphur, and potash

not be assumed that carbonate of lime was replaced by this sulphuret, the pseudomorphs of which really occur.

Silicification is a phenomenon so common, that it is not necessary to assume the existence of any peculiar circumstances during the petrification of stems of trees in the coal formation, which, when standing erect, are but little crushed, and very much so when lying horizontally. This petrifying material is either in an earthy or hard state, coarse or fine-grained; in the latter case, the minutest ligneous fibres can be recognised. In the silicified trees of the coal formation, which are mostly contained in the sandstone strata, the periphery consists of a siliceous, and the bark of a thin carbonaceous mass, while the interior is filled with sandstone. This siliceous mass is, undoubtedly, a chemical deposit from the silica dissolved in sea-water, and the sandstone a mechanical one, like the rock in which the trees are imbedded. The analysis of the former does not show the presence of more than a mere trace of organic matter.\*

The great affinity of silica for organic substances manifests itself in the analysis of rocks containing organic remains, the silica being always found contaminated with them when separated. It is this affinity which causes the separation of the silica dissolved in water penetrating into wood.† If, moreover, it is the case that the organic matter is directly removed by water, it is also probable that the oxygen of sulphates is the decomposing agent.

Sphärosiderite frequently occurs as the petrifying material of

is derived from the large quantity of sea-weed deposited together with clay, and which has penetrated the entire rock; for there are no traces of land plants ever found. In West Gothland, indeed, small beds of true coal are found.

It is worthy of notice, that in the coal formation of Rhenish Westphalia, as well as in the brown-coal beds of the Rhine, iron pyrites and fibrous anthracite are almost constantly associated. See Bischof, German edition, vol. i., p. 923—928.

\* I found a small specimen of petrified wood, from the neighbourhood of Lough Neagh (p. 96), to contain—

Silica	....	....	....	97.71
Alumina and peroxide of iron	....	....	....	0.53
Loss on ignition	....	....	....	0.54
Loss, and organic matter	....	....	....	1.22

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100.00

The petrifying material had an earthy texture; on ignition, only a feeble empyreumatic odour was perceptible, and a slight darkening of colour.

† The analyses of fossil fish bones, by Connel (Edin. n. Phil. Journ., Vol. 17, p. 387, and Vol. 19, p. 300), show that organic matter in any combination precipitates silica from its solution. They contained 10 and 30 per cent. of siliceous matter, and only traces of organic matter.

Calamites in the coal formation, more especially in the shale than the sandstone beds. My son, Dr. Ch. Bischof, and myself, have analysed such specimens from Saarbrücken.

	I.	II.	III.	IV.	V.	VI.
<i>a.</i> { Protocarbonate of iron ... ..	4.05	...	30.28	...	45.86	...
Carbonate of lime ... ..	0.34	...	0.35	...	15.29	...
Carbonate of magnesia ... ..	2.19	...	1.93	...	5.86	...
Peroxide of iron... ..	13.99	...	...	...	...	...
„ of manganese... ..	0.66	...	...	...	3.26*	...
<i>b.</i> { Silica ... ..	51.80	65.76	42.49	76.37	20.75	70.51
Alumina ... ..	14.71	18.67	6.80	12.22	5.49	18.65
Peroxide of iron... ..	2.89	3.67	1.83	3.29	0.83	2.82
Magnesia ... ..	0.29	0.37	...	0.23	0.29	0.99
Water ... ..	4.88	6.20	3.26	5.86	...	...
Loss and alkalis ... ..	4.20	5.33	...	2.03	2.07	7.03
	100.00	100.00	100.00	100.00	99.70	100.00

*a.* Substances soluble in hydrochloric acid.

*b.* Substances insoluble in hydrochloric acid.

I. Analysis of the interior grey mass of crushed Calamites Suckowii, with the cicatrices broken off. It did not grate much when rubbed in a chalcedony mortar, and was easily powdered.

II. Per-centage composition of the part of I, insoluble in hydrochloric acid.

III. Analysis of uncrushed Calamites Suckowii. Black veins intersect the reddish brown mass. It grated very much when rubbed in a chalcedony mortar, and was difficult to powder.

IV. Per-centage composition of the part of III, insoluble in hydrochloric acid.

V. Iron ore with vegetable impressions, from the mine Friederichsthal, near Saarbrücken.

VI. Per-centage composition of the part of V, insoluble in hydrochloric acid.

In the direct determination of water for I and III there was neither any sublimate of decomposed organic matter nor any empyreumatic odour perceptible in the tubes employed, and the silica was perfectly white; consequently, neither of the specimens contained any vegetable matter, all of which had been replaced.

The comparison of II, IV, and VI, with the analyses of shale from the coal-field of Saarbrücken (p. 318), shows that the part of the Calamites insoluble in acid has nearly the same composition as a quartzyl shale.

The abundance of iron-ore in the coal-beds is well known. The

\* Protocarbonate of manganese.

following analyses, when compared with those of the earthy constituents of coal (pp. 267 and 268), furnish us with ideas as to its formation.

	I.	II.	III.
Protocarbonate of iron ....	60·15	27·04	
Carbonate of lime ....	1·53	7·28	
„ of magnesia ....	2·40	2·06	
Sulphate of lime ....	0·29	....	
Silica ....	1·03	31·07	60·66
Alumina ....	6·64	17·48	34·13
Peroxide of iron ....	0·94	....	....
Lime ....	....	0·99	1·93
Magnesia ....	....	0·29	0·57
Potash ....	....	1·39	2·71
Carbon ....	21·27	11·22	
Water ....	4·96		
	99·21	98·82	100·00

I. Analysis of a black shale from a coal-bed near Bochum ; by L. Ch. Hess.\*

II. Analysis of clay iron-stone, full of impressions of shells, forming a bed 6 inches thick in the coal-field of Newcastle. The bed corresponds with another similarly situated in the coal-fields of Derbyshire, Yorkshire, and Scotland, according to H. Taylor.†

III. Per-centage composition of the same ore, after deducting the carbonates, organic matter, and water. When this is compared with the composition of fire-clay (p. 268), it will be seen that there is a very near resemblance ; and it would appear that this mineral is also a mixture of carbonates with clay or shale.

Among the formerly-quoted analyses of the earthy constituents of coal (p. 267) IV, shows some resemblance to the black shale from Bochum. If we imagine the peroxide of iron, in IV, reduced to protoxide, and this, like the lime and magnesia, converted into carbonate, we should then have a substance resembling in composition this black shale, but much richer in iron. It is a question whether the earthy matter of IV would not contain carbonates. This might be decided by testing it with acids.

We have seen that the earthy constituents of the coal, I, II*a*, and III (p. 267), contain, likewise, much peroxide of iron (I, even

\* Poggend. Annal. Vol. 76, p. 113.

† Loc. cit. Calculated from Taylor's analyses.



still more than IV). According to Taylor's researches, the composition of the ash of coal (p. 268) approaches nearly to that of the surrounding clay and shale; consequently, we may assume that the strata associated with the coal,—the ash of which was analysed by Kremers,—may contain large quantities of peroxide of iron. If these strata were strongly impregnated with organic matter, the formation of protocarbonate of iron and other carbonates admits of easy explanation. The organic matter would have reduced the peroxide of iron, enough carbonic acid being thus formed to convert  $\frac{1}{4}$  of the protoxide into protocarbonate. Then, as carbonic acid is also formed, in the conversion of vegetable remains into coal, there would have been no deficiency of this acid for the purpose of forming carbonate with the remaining  $\frac{3}{4}$  of the protoxide of iron.

It is thus shown that the formation of coal, protocarbonate of iron, and other carbonates, may have gone on simultaneously; but at the same time it must be understood that such a formation of carbonates could also have taken place after the coal formation was raised above the sea; for, in contact with organic matter, the reduction of the peroxide of iron advances so long as there is the least trace remaining. The carbonates in the fissures of coal (p. 266, note) are, undoubtedly, such subsequent formations. It is self-evident that the formation of sphærosiderite in the Calamites would have taken place in precisely the same way, at the cost of their vegetable matter, if they had been filled with sediment which was as rich in peroxide of iron as the above ashes of coal.

All that has been said in reference to the origin of the clay iron-ore in the coal basins will also apply to the formation of that occurring in brown coal-beds. A bed of clay in that formation, which was as rich in peroxide of iron as the ash of the brown coal, V (p. 267), would have yielded a considerable quantity of protocarbonate of iron.

Quartz, in its several modifications of chalcedony, hornstone, &c., occurs with the forms of calc-spar, as do iron-spar, and even iron pyrites, these two being frequent petrifying materials of plants. Carbonate of lime may therefore be displaced by them. Although carbonate of lime is not frequently present in the ashes of coal, there are some which contain as much as 20 per cent., and still more (p. 266, note); and the clay-iron ore II (p. 314) likewise contains this carbonate. It is therefore admissible to suppose that the original substance of the plants was petrified by carbonate of lime, which was subsequently displaced by some one of the above substances, espe-

cially protocarbonate of iron, long after the elevation of the coal-basins above the sea. The analysis of a specimen of fossil wood, from the sandstone quarry of Craigleith, by R. Walker,\* according to which it contained 50·36 carbonate of lime, 24·65 protocarbonate of iron, 17·71 carbonate of magnesia, and 6·15 carbon, silica, and water, shows that several carbonates together may form the petrifying material. But it is also possible that carbonate of lime was the original petrifying substance, and that it was afterwards partially displaced by carbonate of iron and manganese. The separation of carbonate of lime by vegetable agency, really observed (p. 189), favours this view in the highest degree.

Besides the above-mentioned petrifying substances, no others have yet been met with in the coal formation; but wood has been found in newer formations, petrified by gypsum and baryta spar. (Chap. XX.)†

The incrustations of extinct plants occur less frequently than petrification by impregnation. The fragments of plants then form impressions in the incrusting substance, and are themselves converted into a brown powder. It is very rarely that their interior organic structure can be recognised. Silica and carbonate of lime are the substances which, in solution, have generally formed the incrustation, but suspended matter—shale and clay-slate,—have given rise to the formation of casts, and indeed most frequently.

The stems of trees occurring in the coal formation, partly in a perpendicular position, filled inside with the same rocky substance that they are imbedded in, and with the bark converted into coal, are of especial interest.‡ Nöggerath§ has carefully collected all that was known with reference to this subject, and added an

\* Edinburgh new Philos. Journ.. Vol. 18. p. 363.

† It is worthy of notice, that the wood is converted into pitch coal, where it is petrified by baryta spar. This coal lies also in the midst of baryta spar.

‡ According to Göppert (Zeitschrift der deutschen geolog. Gesellschaft, Vol. 3, p. 294), clay ironstone occurs in the coal formation of Upper Silesia; a very soft shale, which soon falls to powder in the air in Lower Silesia; a more or less coarse-grained sandy conglomerate in the transition rocks, near Landshut, in Silesia, as the substance filling the interior of the stems. It is on this account that, in the former places, the natural round form of the stems is best preserved. In Upper Silesia, the bark of the stems, as well as the axis of the interior, consist of a closely-adhering coaly mass. In the transition rocks of Landshut, there is found, as on all the stems occurring there, only a slight anthracite dust, which is easily removable. The preservation of the barks of these trees is owing to the fact, that the tissues of that part, as in trees now existing, resist decay the longest. Göppert (Poggend. Ann. Vol. 86, p. 483,) macerated *Arum arborescens* for six years, and found that at the end of that period the bark was in a perfect state of preservation, while the vascular tissues had entirely disappeared.

§ Ueber aufrecht im Gebirgsgestein eingeschlossene fossile Baumstämme, 1819. Fortgesetzte Bemerkungen, 1821.

account of some new observations made at Wellesweiler in the coal-field of Saarbrücken. Between two seams of coal, separated by a stratum of sandstone and sandy shale, 49 feet thick, the stem of a tree, 9 feet 8 inches high and 13 or 18 inches thick, was found standing in an erect position in the centre of the above-named stratum. Subsequently, seven other petrified stems of a similar kind were found at other spots, two of them having several impressions of plants\* in their interior, in some parts also, rush-like stalks, with a thin coating of coal. One of these tree-stems, without roots, but also without any distinct separation from the rock, stood in shale, as far as it was possible to judge, about 14 or 21 feet above a coal-seam. Another stem, likewise standing in shale, rested immediately upon a coal-seam  $\frac{1}{2}$  an inch thick, under which was again shale. In the coal-mine, Kohlwald, three miles from Wellesweiler, a tree-stem measuring  $2\frac{1}{2}$  feet in diameter and  $8\frac{1}{2}$  feet in height, was found standing in shale between two coal-seams. In the mine, Geislautern, a petrified stem was found which is said to have been about 3 feet in diameter; it stood immediately upon a coal-seam, but no traces of roots could be discovered in the latter.

Schmidt† has described an erect petrified stem, about 7 feet high, which was found in a bed of sandy shale of the same height at Kloster Rumbeck, near Arnsberg; a bud, converted into sphærosiderite, was attached to it, almost in contact with the carbonaceous sandstone resting upon the shale. The brush-shaped root was scarcely perceptible. Graf von Sternberg‡ gave a description of a fossil-stem in an erect position, but without roots, which was found in Radnitz (Bohemia). The lower end was in contact with shale, which rested upon a coal-seam 4 inches thick.

Hawkshaw§ described five fossil trees exposed in a cutting on

\* Von Schlottheim (Beiträge zur Flora der Vorwelt, p. 21) also mentions such impressions of plants in petrified stems of trees. I found in the interior of a hollow beech, which still vegetated vigorously, a number of roots grown to the sides, one of which was about a quarter of an inch thick. They extended throughout the pulverulent decayed wood. Stalks in petrified trees may, therefore, result from the growth of such roots. Large quantities of leaves are always found in hollow trees.

I am not aware that this phenomenon has yet been noticed by botanists. Nature appears to make use of this means to convey nutriment to such decayed trees, and, indeed, at the cost of their own decayed wood. It may therefore be on this account that, although frequently only the bark of these trees remains, vegetation still goes on. This circumstance is, perhaps, sometimes the cause of the considerable decrease in the volume of wood, when stems of trees suffer decay in their interior (p. 285).

† Nöggerath. Loc. cit., p. 52.

‡ Ibid., p. 41.

§ Proceedings of the Geological Society of London. No. 64 and 69.

the Manchester and Bolton Railway, standing erect in relation to a bed of coal, and with their roots in a corresponding position. The largest of these was 5 feet in diameter at the base, and 11 feet high.

Some years since a number of forest trees were found in making a cutting for the Saarbrücken and Bexbach Railway. One of these stems, retaining its roots and measuring 9 to 11 inches in height, and 15 to 21 inches in diameter, is now in the Museum at Bonn. It stood erect, 28 feet below the vegetable soil, upon a bed consisting of argillaceous sandstone and shale, which covered it to a height of 8 feet.\*

The composition of a piece of the root of this stem and of several shales from the coal field of Saarbrücken is according to my analyses, the following:—

	VII.	VIII.	IX.	X.	XI.
Silica ....	62·37	67·35	68·50	72·94	75·01
Alumina ....	18·64	20·66	18·10	16·66	17·57
Peroxide of iron ....	7·82	2·55	3·62		1·02
Protoxide of iron ....				5·61	
Lime....	0·12	traces	traces	....	0·23
Magnesia ....	0·57	0·60	0·81	0·85	0·24
Organic matter ....	1·51	....	....	2·20	
Water, and loss by ignition ....	4·76	6·70	7·78	0·75	6·30
Alkalies and loss ....	4·21	....	....	1·40	
	100·00	97·86	98·81	100·46	100·37

VII. Analysis of the substance filling the stem. The quantities of organic matter are rather too small, for the silica contained some when separated.

VIII, IX, and XI. Shales in the underlying strata of the coal seams; X from the middle of a coal seam; XI was almost white; VIII and IX were coloured grey by carbonaceous particles, and X was pale green.

The composition of VII so closely resembles that of the shales, that it can only be regarded as shale with the smallest per-centage of silica. This stem, therefore, can only have been filled by the matter suspended in water, and there can be no doubt, that the same was the case as regards all other stems of this kind.

\* Göppert, in the Zeitschrift der deutschen geologischen Gesellschaft. Vol. 3, p. 285. He describes another fragment of a tree stem from the coal formation at Waldenburg, which was filled with shale substance, and covered with a wrinkled bark presenting the cicatrices of stigmata.



There is a difference of opinion as to how these petrifications by mechanical means have been produced. Nöggerath and several others are of opinion that the trees grew near the spots where they are found and often actually in the same place. Joh. v. Charpentier\* is, on the contrary, of opinion that they have been transported to where they are found.

According to the former view, a long space of time would have elapsed between the formation of the strata upon which the trees grew, and the formation of those in which they are found imbedded, requisite for the growth of such thick stems. During this growth the former strata would have been above the sea, and subsequently sunk beneath it. No observations, which have hitherto been made, show any distinct boundaries between the strata upon which the trees are supposed to have grown, and those in which they are now imbedded; consequently the materials from which they were both formed must have been identical. Even though the frequently immense beds in the coal formation indicate a uniformity, during long periods, in the character of the suspended earthy matter from which they were formed, still it appears probable that there would have been some recognizable difference between strata whose dates of formation, according to this view, were so far apart.

Let us imagine that a stratum of uniform thickness, perfectly horizontal and covered with vegetation were to sink with such regularity as to retain its horizontal position even beneath the sea; let us suppose the thickness of this stratum to be uniformly increased by the deposition of mineral matter from the sea water, the original parallelism of the strata would not in this case be disturbed. But if a stratum covered with vegetation were to sink in such a manner beneath the sea, as to assume an inclined position, and then be covered uniformly with new deposits, these would not be parallel with the older stratum. The strata of the coal formation retain their thickness for long distances, so that such a want of parallelism might be easily detected. The relative parallelism or non-parallelism of the older and younger strata would remain undisturbed by any subsequent elevations or depressions of the entire coal formation. Uniform motions of this kind are extremely rare, as is shown by the tilted strata and the elevation of Sweden. It is therefore to be expected, that the floor and roof of any stratum, containing erect stems of trees, would more frequently be wanting in parallelism than the reverse.

Whether such a want of parallelism has ever been observed at

\* Bibl. universelle. 1818. Vol. 9, p. 254.

any spot where stems of trees are found, I do not know. Should such geognostic relations anywhere present themselves, they would afford evidence that the trees had actually grown upon the spot where they were found. But if the floor and roof of strata containing trees are in all cases parallel, this fact is evidence in favour of the contrary view. It is therefore greatly to be desired, that geologists should study the geognostic relations of such strata as contain and are associated with fossil trees in an erect position, as far as may be possible.

Wherever there is vegetation, vegetable mould is formed. All the leaves and twigs, which in a primitive forest fell from the trees and decayed, yielded it. Even if there was only one growth of trees upon the shale, there would have been by no means an inconsiderable bed of vegetable mould, which, when sunk below the sea, would have been converted into coal. This bed must have been beneath the lower end of the stems of the petrified trees, as is shown by trees whose roots are laid bare by the fall of earth. Wherever such seams of coal occur, even when they are only a few inches thick, there is a probability that the fossil trees have grown upon the spot where they are found. When they are not found, it may be assumed that the vegetable remains have been washed away during the sinking of the land beneath the sea. In this case, there must have been a violent motion in the sea at the time that this sinking took place; for if it had taken place in still or slightly agitated water, the vegetable remains would soon have been covered by the mechanical deposit. Depressions of land may be regarded in some cases as the results of earthquakes, and it is possible that there may be a causal connection between them and a violent agitation of the sea. But as earthquakes have but a short duration, the agitation of the sea would not have continued long enough to have caused the denudation of a thick bed of vegetable remains. If the water came to rest shortly afterwards, the deposition of sediment would at least have recommenced before all this vegetable matter was washed away, and traces of it would still be recognized upon the roots of the fossil trees.

The very frequent erect position of fossil trees appears to lend essential support to the view, that they have grown on the spot where they are found. Nevertheless, it has already been shown, by many examples, that stems in an erect position, are actually found in drift wood. Moreover, it may be proved, that under certain circumstances, they must necessarily reach the

bottom of the sea in this position. The centre of gravity in a tree, hollow as far as its roots, is below the point where the cavity ends. Such a tree would float erect, and indeed in a perfectly perpendicular position, if the roots on opposite sides were of equal length and thickness. This case would certainly be rare; the floating trees would generally have a more or less inclined position. When perfectly saturated with water, they would sink and reach the bottom in the position in which they floated. If the roots were all in the same plane, and if the bottom of the sea were horizontal, the tree would settle in an erect position, even when it did not float so. When these conditions did not exist, the position of the trees would deviate more or less from the perpendicular.

In the fossil tree above (p. 318) mentioned, the distance between the longest roots is rather more than twice as great as its diameter, and  $3\frac{1}{2}$  times as great as its height. The centre of gravity would therefore have been below the middle, even if it had not been hollow. Such a stem could only float upright, and must have reached the bottom in this position.

A fir-stem,  $2\frac{1}{4}$  inches in diameter, was cut off  $2\frac{1}{2}$  inches above the roots; it had a central root 7 inches long, and the distance between the ends of the longest roots was 12 inches. It floated erect in water, although not quite perpendicularly, because one of the roots was much thicker than the others. When the middle root was somewhat loaded, the stem sank and stood upright upon the bottom of a pond.

Stems with small roots, and of considerable length, in which the centre of gravity is far above the roots, cannot float upright, still less stems without roots, and unless they happen to be jammed in between large masses of driftwood, can only reach the bottom in an horizontal position. If then such long thin stems, with or without roots, are found upright in the strata of the coal-formation, as in the sandstone of the mine of Treuil near St. Etienne, there is no possibility of supposing that they sunk during the deposition of these rocks. When, on the other hand, fossil trees occur in all kinds of positions, as in the roof of the Appalachian coal-fields and other places, the opinion that these trees have been transported there as driftwood, has a higher degree of probability. In the submergence of a primitive forest, only those trees which were fixed to the ground by their roots could have retained their position. The broken and loose stems would have floated; and if at a subsequent period they sunk, they certainly could not have assumed an oblique position.

Taking all these circumstances into consideration, the only conclusion we can come to is, that fossil trees have originated partly from submerged forests, and partly from floating drift-wood. There are no grounds for regarding this as impossible, for submerged forests and floating trunks of trees are well-known phenomena.

Although, as Hawkshaw correctly observes, large trees can scarcely have been hollow tubes originally, still we must agree with Nöggerath in the opinion, that those trees which are found filled with sedimentary substances, had at least become hollow by decay. From the character of these trees we may infer, that at the time of their growth, a warmer climate prevailed at the spots where they are found than at the present time; consequently, the wood of trees broken down by storms must have decayed very quickly, while their bark was able to resist the decomposing influences for a much longer time.

Nevertheless, I cannot altogether doubt that plants which, like Calamites, contain large cells, may be filled with sediment. If the suspended matter in water passes even through filtering paper, it may also penetrate into cells, and be deposited there; but whole plants and stems, such as we find in petrified trees, cannot penetrate into the cells.

Submerged forests occur at many places. Lyell\* mentions some instances. These forests must have been brought into their present position by a general sinking of the ground on which they grew. Such a forest has been traced for several miles along the northern shore of the county of Fife, and is covered by stratified clay, from 15 to 20 feet in thickness. There can be no doubt, that any hollow trees, which must have existed in these forests, would have been filled with clay. But if these submerged forests were again raised above the level of the sea, what would be the appearance of the original and subsequent strata? Those trees only which were hollow before the submergence, would be filled with clay; those which were not hollow, and whose number, to judge from the usual proportion of them in our present forests, must have been far greater than that of the hollow trees, would have been converted into a carbonaceous substance. Both the trees filled with clay, and those which were carbonized, might have retained their erect position. If, however, the submergence of a forest took place so gradually, that the trees remained for a long time exposed to the action of the tides, they could hardly have

\* Principles, p. 238, 309, and 719.



retained this position, but would have been thrown down in all directions. It cannot be doubted that the hollow trees would have been filled with sediment in this case likewise.

An objection might be made to the opinion, that trees filled with sediment have originated from submerged forests, inasmuch as such trees are only found singly, while it is certain that the ancient forests were as densely crowded with trees as those of the present time. However, when it is remembered that the strata lying between coal-seams are seldom worked in coal-mines, and consequently that petrified trees are only found under accidental circumstances, no great importance can be attached to this objection; moreover, in the cutting upon the Saarbrücken and Bexbach Railway such a number of petrified trees have been found that they appear like a forest.

When decayed trees, filled with pulverulent decayed wood, are carried into the sea, this is washed out and sinks. The hollow trees themselves sink after a while, for decayed beech-wood sinks in water, even in large pieces (p. 296). They would sink the more readily when their roots were loaded with stones and other heavy matter. In this case they would naturally sink with their branches upwards; thus snags, or trees with their roots downwards, and forced along by the current in a vertical position, are common in the Mississippi, and during the *débacle* of the Vallée de Bagnes trees were forced down the valley and left standing with their roots downwards at Martigny.\* It is evident that suspended matters would be deposited in, as well as around, such erect hollow trees situated at the bottom of the sea; and the fact that trees in forests are not unfrequently so hollowed out, that scarcely anything remains but the bark, agrees with the mode of occurrence of fossil trees whose bark is converted into coal. The above-mentioned fossil trees on the Manchester and Bolton Railway belong, according to Robert Brown, to the Coniferæ, and we cannot therefore account for their petrification, except by supposing their interior was first removed by decay.

Another circumstance connected with these trees is difficult to explain: the hollow trees in forests have sound solid roots; but the roots of the fossil tree in the museum at Bonn, as well as probably all fossil trees, are filled with shale to the very ends. So long as there is no better explanation of this fact offered, we may regard the sulphate of lime present in sea-water as the agent by which the vegetable matter has been displaced from the roots

\* De la Beche, Geological Manual, p. 428.

(p. 310). The carbonate of lime, which resulted from the mutual decomposition of sulphate of lime and ligneous matter, may have been removed by the carbonic acid in sea-water, while the suspended shale substance was deposited in its place; but if such a process went on in the roots, it is also possible that it may have taken place in the stems, and those trees which were not originally hollow may have been filled with sediment in this way. Still, however, we must assume the existence of unknown special conditions under which vegetable tissues are decomposed by sulphate of lime, for if this process were a general one there could not have been any formation of coal in the sea.

The above attempted explanation is applicable whether the trees are found at the spot upon which they grew, or whether they have sunk in the sea. In the former case, as the roots were still buried in the ground, the sea-water would have had more limited access to them than in the latter; however, this difference would not cause any greater difficulty in explaining the petrification of the roots. But the circumstance already mentioned, that the sedimentary substances present in the sea during two periods far distant from each other must have been identical, is opposed to such an assumption. Certainly the simultaneous formation of the rock which fills the decayed roots, and that surrounding them, is more easily conceivable than the reverse.

The conversion of vegetable substances into coal is not unfrequently combined with a petrification. Brown stony pieces are sometimes found among brown-coal, the carbon of which will not burn of itself, but only in the fire, by means of which the organic texture is rendered perceptible. Moreover, the external forms of many such fragments show that they are remains of the trunks and branches of arborescent plants; these half-carbonized and half-petrified masses occur in almost all formations, and accompany the coal-seams in the roof and floor of thin shale and grit beds. Many of the petrified woods occurring in the transition rocks, and even the small carbonized fragments of plants in fresh-water limestone, are likewise of this kind; they differ from the perfectly petrified vegetable remains, in having suffered only a partial replacement of their organic constituents by inorganic materials.

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## CHAPTER XVI.

## EXHALATIONS OF SULPHURETTED HYDROGEN AND SULPHUROUS ACID.—SULPHURIC ACID AND SULPHUR.

SULPHURETTED hydrogen is almost always present in volcanic exhalations, when they pass into the condition of solfataras. It is exhaled from sulphuretted springs, together with carbonic acid, nitrogen and sometimes also carburetted hydrogen, and has frequently been met with in boring artesian wells. It is likewise evolved during the decay of organic matter, either when containing sulphur, or when in contact with sulphates. Exhalations of this gas are, therefore, very common phenomena.

Sulphuretted hydrogen cannot be formed from any inorganic substance without the aid of water. In nature it always occurs associated with water, either absorbed, as in sulphuretted springs, or mixed with steam, as in the solfataras. It cannot be disengaged from ignited masses, because it is decomposed by heat; this is the reason why it is met with in the smoke of solfataras, but not in the smoke of Vesuvius.\*

Sulphuretted hydrogen may be obtained artificially from several metallic sulphurets. According to my experiments, it is also disengaged from soluble sulphurets by boiling them with water. A slip of paper, moistened with acetate of lead, acquires a distinct brown colour when laid upon a dish in which sulphuret of calcium is mixed with water heated only to  $111^{\circ}$  F.†

The question now arises how sulphuretted hydrogen is formed in nature. When it is remembered that sulphuretted springs issue from, or in the neighbourhood of, coal-beds, bituminous rocks, marshy ground, &c., all of which are highly charged with organic remains; that organic matter is present in every mineral water; and, finally, that there are sulphates in all the sulphuretted mineral waters which have hitherto been examined; it will be evident that in these localities there are all the conditions necessary for the formation of sulphurets and sulphuretted hydrogen. The facts above (p. 15, No. 27) mentioned are quite sufficient

\* Monticelli and Covelli, *Der Vesuv.* German Transl., p. 171.

† Germ. Ed. Vol. 1, p. 654; and Vol. 2, p. 157.

to explain the formation of sulphuretted hydrogen and sulphuretted water.\* This gas is consequently evolved wherever water containing sulphates comes in contact with organic matter. Among other places, it is found in coal-mines which have been abandoned, when the water penetrating into them contains gypsum.†

According to Lewy,‡ the sea-water from the coast between Langrune and Lyons contains minute quantities of sulphuretted hydrogen, and, as it appears, in constant quantities which amount in the morning to 0·30, in the evening to 0·32 cubic centimetres in a litre of water. If the water is taken from pools in which it is left by the receding tide, the quantity of sulphuretted hydrogen varies in proportion to the number of marine animals present, especially shells, which so frequently cover the bottom of these pools in large quantities. Water from pools which are apparently without marine plants or animals never contains more than 0·33 cubic centimetre of sulphuretted hydrogen, while that in pools lined with shells contains 1, 2, 3, or even 7 cubic centimetres in the litre. Here likewise there is an evident reciprocal action between sulphates and organic matter.

It cannot be doubted that the water of rivers flowing into the sea contains metallic salts, although in very minute quantities; and it would appear to be a wise provision that in the sulphuretted hydrogen of sea-water there should be a precipitating agent capable of separating the minutest traces of these metals, thus preventing the gradual accumulation of substances prejudicial to animal life.

The formation of sulphuretted hydrogen is likewise possible in rocks destitute of organic remains, if the meteoric water conveys these to them from sedimentary strata or from vegetable mould, for sulphates are very frequent constituents of crystalline rocks. The water of the sulphuretted springs in the granitic district of the Pyrenees contains organic matter in solution, in the form of baregin.

Organic matter may sometimes be the cause of the presence of sulphuretted hydrogen in the solfataras. The solfataras of Puzzuoli continually exhales with violence aqueous vapour.§ The

\* Twenty-four years ago I observed this change in a striking manner. *Jahrbuch der Chemie. und Physik.* Vol. 57, p. 26, and Vol. 64, p. 377.

† Accidents are not unfrequent in such mines. A few years since some miners were suffocated in entering such a mine in the neighbourhood of Aix-la-Chapelle.

‡ *L'Institut*, 1846, No. 665. For remarks upon the effluvia at the mouths of rivers whose water is loaded with organic matter, and which fall into the sea. German Ed. Vol. 1, p. 656.

§ Posthumous works of Fr. Hoffmann. Vol. 2, p. 466.



water penetrating to the focus of this extinct volcano, whether it be sea or meteoric water, contains organic matter. Sea-water contains, besides this, sulphates; consequently there are present all the conditions for the formation of sulphuretted hydrogen, and it is further favoured in the solfataras by the high temperature.

The production of sulphuretted hydrogen by the gradual decomposition of sulphates, by means of organic matter, is a very slow process. When only the carbon of the organic matter combines with the oxygen of the sulphate, twice as much carbonic acid is formed as is necessary for the disengagement of the sulphuretted hydrogen. In this case carbonic acid must always be exhaled, together with the latter gas; and it has, indeed, been found in all the waters and exhalations from sulphuretted springs which have yet been analysed. All these processes consist essentially in the formation of an alkaline or earthy sulphuret, by the decomposition of sulphates by means of carbonaceous substances, and the subsequent decomposition of the sulphuret, from contact with water and the carbonic acid generated in the first part of the process; for when carbonic acid is passed through a solution of sulphuret of sodium or calcium, sulphuretted hydrogen is disengaged.

The disengagement of sulphuretted hydrogen from alkaline and earthy sulphurets, by aqueous vapour (p. 325), is a process which must be taken into account in explaining the production of this gas, when occurring mixed with steam, as in the solfataras and hot sulphuretted springs. Even other metallic sulphurets—sulphurets of lead, silver, and copper—evolve sulphuretted hydrogen when in contact with steam at a moderately high temperature.

The temperature of boiling water, which, under ordinary circumstances, is very far below the surface of the earth, is, in volcanic districts, much nearer. It may therefore happen, in such places, that sulphurets but little below the surface yield sulphuretted hydrogen, in consequence of contact with aqueous vapour. Alkaline and earthy sulphurets have actually been found in lavas, and it is therefore very probable that the sulphuretted hydrogen of the solfataras is formed in this way.

When the water penetrating into the earth contains atmospheric air, nitrogen may also be present in the exhalations, together with the sulphuretted hydrogen and carbonic acid, which is indeed the case in most sulphuretted springs. If the organic substance which gives rise to the formation of these springs is nitrogenous, nitrogen is produced by its decomposition.\* Carburetted hydrogen

\* With regard to the co-existence of oxygen and sulphuretted hydrogen in sulphuretted springs, see German Ed., Vol. I, p. 662.

sometimes accompanies sulphuretted hydrogen in exhalations. According to Du Menil, this is the case at Eilsen. According to Hericart de Thury, both gases were evolved from springs bored in carbonaceous marl containing sulphates, at Argenteuil, in France.

The gases which escape from the volcanos of the equatorial zone in America contain, according to Boussingault,\* besides a large quantity of aqueous vapour, carbonic acid, and sulphuretted hydrogen. The former gas, however, always preponderates so much as to amount to 140 or 1000 times as much as the sulphuretted hydrogen. The gases exhaled from the neighbouring springs are stated, by the same authority,† to correspond in composition with those from the volcano. Daubeny is of opinion that this is always the case. The researches of Humboldt‡ upon the interior of Asia have made us acquainted with the largest of all known solfataras, situated near the town Urum-tsi, in Chinese Tartary. According to many concurring statements, it is 30 miles in circumference. The solfatara of Dafane, in Abyssinia, likewise appears, according to Rochet,§ to be very extensive.

Bunsen|| examined the following exhalations, occurring in Iceland:—

	I.	II.	III.	IV.	V.	VI.
Carbonic acid ....	87.43	88.24	88.54	86.92	79.07	30.00¶
Sulphuretted hydrogen....	6.60	6.97	1.79	3.28	15.71	24.12
Hydrogen ....	4.30	4.10	7.87	8.36	4.72	25.14
Nitrogen....	1.67	0.69	1.80	1.44	0.50	0.72
	100.00	100.00	100.00	100.00	100.00	99.98

I, from the solfatara of Krisuvik. This exhalation consists of 82.30 of aqueous vapour, and 17.70 of gases. It is therefore probable that the latter occurs only in small proportions in the other exhalations.

II, from a hot spring in the neighbourhood of the former.

\* Annal. de Chim. et de Phys. Vol. 52, p. 5. Boussingault examined the gases from five volcanos.

† Ibid., p. 181.

‡ Ritter, Erdkunde. Vol. 2, p. 386.

§ Comptes rendus. Vol. 12, No. 21.

|| Poggend. Annal. Vol. 83, p. 245, et seq.

¶ There is a misprint here, which decreases the total sum by 20. One of the constituents, apparently the carbonic acid, has been stated too low by 20 per cent.

III and IV, from small boiling springs in the midst of the solfatara of Krisuvik.

V, from an exhalation in the neighbourhood of Reykjavik.

VI, from an exhalation at Reykjahlidh, in the north of Iceland.

Some of these exhalations rise with so much force as to throw out pieces of rock of from 3 to 4 inches in diameter. Although these exhalations, like those of the equatorial zone in America, contain much more carbonic acid than sulphuretted hydrogen, yet the former exceeds the latter only to the extent of from 5 to 49 times. The products of decomposition in the rocks surrounding the exhalations contain no carbonates, for decompositions are effected only by the sulphuretted hydrogen. Since the exhalations contain no carburetted hydrogen, Bunsen supposes that they cannot be derived from organic remains. When the vapour of sulphur comes in contact with heated rocks containing augite, sulphuret of iron is formed from the peroxide of iron, and sulphurous acid is evolved. If the rocks should now be acted on by aqueous vapours, sulphuretted hydrogen would be disengaged (p. 325); and if the temperature should a little exceed that of a low red heat, this gas would be decomposed and hydrogen evolved, along with sulphurous vapours. In this manner Bunsen explains the presence of hydrogen in the exhalations mentioned; and, according to him, there are compounds of sulphur which, when exposed to the volcanic heat, afford the sulphur for the decomposition of rocks containing augite. Since iron pyrites is the sulphuret chiefly decomposed by heat, and since it occurs, not only in veins and layers, but also in rocks, this substance may, according to my view, be considered as the probable source of the disengagement of sulphurous vapours.

When we compare the exhalations of carbonic acid with those of sulphuretted hydrogen, great differences are found. The former generally consist of nearly pure carbonic acid (p. 233); but there has never yet been an exhalation of the latter gas in an unmixed state met with; it is generally mixed with others, in such a small proportion as only to be recognisable by its smell. The gases with which it is associated cannot be accidental admixtures, because they are always found, and must therefore be intimately connected with the formation of sulphuretted hydrogen. Since, in the decomposition of sulphates by organic matter carbonic acid appears as a result, and in the decomposition of the sulphurets formed it acts the part of a cause, we may infer, with the greatest probability, that this process really does take place. If the sulphuretted hydrogen

was disengaged from sulphurets by other acids, we should meet with it as pure as when prepared artificially. But as it has never been observed in this state, it appears that no such disengagement ever takes place in nature.

Dumas\* could not recognise either sulphurous acid or sulphur as products of the slow oxidation of sulphuretted hydrogen, but only sulphuric acid. But when it burns with flame, water and sulphurous acid are formed, and almost always a precipitate of sulphur and traces of sulphuric acid. Further, if sulphuretted hydrogen is absorbed by water which is exposed to the atmosphere, sulphur is precipitated, as is seen in sulphuretted springs. This likewise occurs when sulphuretted hydrogen is mixed with aqueous vapour, as in the solfataras, for a sulphuretted water is formed by the condensation of the vapour. Breislak† observed at the solfataras of Puzzuoli, that if the sulphuretted hydrogen was not considerably heated when it came into contact with atmospheric air, no sulphur was deposited, but sulphuric acid was formed. If sulphuretted hydrogen were disengaged as pure as carbonic acid, and with as little admixture of aqueous vapour, it would be entirely converted into sulphuric acid. If, as Dumas has shown, porous bodies facilitate this change, it would go on more readily in contact with limestone, and give rise to the formation of gypsum.

On the other hand, the formation of sulphuric acid takes place less readily the smaller the proportion of sulphuretted hydrogen mixed with the aqueous vapour; for the more the latter preponderates the more readily is sulphuretted water formed by its condensation, and sulphur is then separated. A proportionately larger quantity of sulphur is deposited, the smaller the proportion of sulphuretted hydrogen mixed with the aqueous vapour. This is a very important circumstance, for it shows not only that a minute quantity of sulphuretted hydrogen, mixed with aqueous vapour, does not prevent the formation of sulphur deposits, but, on the contrary, that such vapours, weakly impregnated with the gas, when they are evolved during a sufficient length of time, yield larger deposits of sulphur.

Boussingault‡ found, in the volcano of Cumbal, sulphuretted hydrogen only in the higher parts, where the temperature of the fissures did not exceed 185° F.; in the hotter fissures, sulphurous

\* L'Institut. No. 669. 1846.

† Lehrbuch der Geologie. German Translation. 1820, Vol. 2, p. 262.

‡ Loc. cit.



acid. Humboldt\* made similar observations previously in the fissures of the Purace. He also† saw, from the lofty summit of Rucu-Pichincha, that at a considerable depth in the crater, blue flames moved about, and he distinctly recognised the smell of sulphurous acid. Probably the flames were those of burning sulphuretted hydrogen.‡ Daubeny§ has ascertained that the vapour of the solfatara on the island of Vulcano consists of sulphurous acid; at the external surface of the crater, of sulphuretted hydrogen.

The formation of gypsum from limestone in the neighbourhood of exhalations of sulphuretted hydrogen is a very common phenomenon. Breislak|| brings forward many examples of such a formation near sulphur springs. In 1823, Covelli¶ found very beautiful crystals of gypsum and sulphur in the crater of Vesuvius, originating from the fumaroles. Dumas has shown that even the most minute traces of sulphuretted hydrogen convert limestone into gypsum. He found no free acid in the fumaroles of Tuscany, and yet the carbonate of lime in their neighbourhood was rapidly converted into gypsum, which could only be owing to a minute quantity of sulphuretted hydrogen in these vapours. He observed a similar phenomenon in the sulphur baths at Aix. The limestone walls of the saloons and bath-rooms blister, and become covered with crystals of gypsum.

In the Lipari islands, vapours impregnated with sulphuretted hydrogen have given rise to the formation of very extensive masses of gypsum.\*\* The entire tuff, near the Fumerole di St. Calogero, in the island of Lipari, is intersected with snow-white or pale red fragments of gypsum, and is very frequently covered with a crust of this substance. Deposits of gypsum occur in many other parts of this island, as well as in Vulcano, under similar circumstances. This is by no means an insignificant phenomenon, but extends almost entirely throughout a coast several miles long. The height of the cliffs penetrated by gypsum is frequently 200 feet and even more. Hoffmann does not make any mention of the occurrence of sulphur in this gypsum district. The proportions of sulphuretted hydrogen to aqueous vapour in these fumaroles appear therefore to

\* Annal. de Chim. et de Phys., Vol. 27, p. 129.

† Poggend. Annal., Vol. 44, p. 214 and 217.

‡ German Edition. Vol. 1, p. 665.

§ A description of active and extinct volcanoes. Second Ed. 1848, p. 256.

|| Loc. cit. Vol. 2, p. 264.

¶ Poggend. Annal. Vol. 10, p. 496.

\*\* Fr. Hoffmann, in Poggend. Annal., Vol. 26, p. 1, et seq.

have been such, that the whole of the sulphur was oxidized to sulphuric acid; it therefore resembles the experiment of Dumas, in which he was unable to recognise sulphur.

The decomposing action of the sulphuretted hydrogen in fumaroles cannot be supposed to consist in its penetration of the rocks from below, for in that case the quantity of oxygen necessary for its oxidation would be wanting. It cannot be doubted that the vapours of the fumaroles in Lipari, condensed upon the rocks adjoining, are there oxidized, and thus give rise to the formation of gypsum in a manner precisely similar to that observed upon the walls at Aix. Rain assists this action, and conveys the sulphuric acid already formed into the interior of the rock.

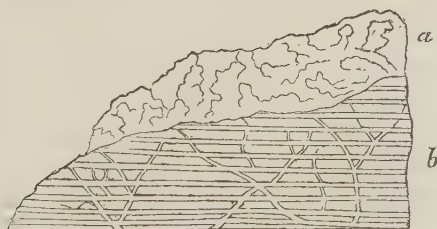
This change perfectly resembles the decomposition of rocks by the penetrating of the meteoric water. In the one case carbonic acid is the chief chemical agent, in the other the more powerful sulphuric acid. But the sulphuric acid in the condensed vapour of the fumaroles is undoubtedly in a more concentrated state than the carbonic acid of meteoric water. It is therefore easy to perceive why the sulphuretted fumaroles effect the decomposition of rocks in a much shorter time than meteoric water. But the latter is capable of bringing about, in a proportionately longer time, all the effects of the former. The change which in one case we see as if it were going on under our eyes, admits of our inferring the nature of those which we cannot actually trace.

Upon the island of Lipari there is a lava-bed converted, by the waters containing sulphuric acid penetrating into it, into a compact, coarse-grained, and perfectly colourless rock. Although the iron is removed, and deposited in the surrounding tuff, and siliceous masses were separated, the rock did not crumble down. These are phenomena precisely analogous to those which occur in crystalline rocks which are merely exposed to the action of meteoric water containing minute quantities of carbonic acid and oxygen. Carbonated meteoric water converts silicate of lime into carbonate of lime, in the same way that water containing sulphuric acid converts the same mineral into sulphate of lime. The carbonate of lime which we find in such rocks as lava or basalt, and which can frequently only be detected by the effervescence with acids, is certainly nothing more than the product of such a decomposition.

It is an important fact that the gypsum is distributed partly in detached fragments, partly in nodules or laminae, although there can be no doubt that the lime from which it was formed was distributed throughout the entire mass of the tuff. This clearly shows that in

the decomposition and alteration of rocks, a disseminated substance segregates in consequence of its combination with the decomposing agent; and this throws a light upon other metamorphic processes, which we cannot follow so closely as those caused by fumaroles. For instance, if we find in some basalts and wackes iron-spar in well-developed crystals, we must regard its formation as being quite analogous to that of gypsum, above described; in the one case, carbonic acid being the substance which imparts chemical activity to the percolating water, and enables it to convert proto-silicate of iron into protocarbonate; in the other, this substance is sulphuric acid, and gypsum the product of its action upon calcareous minerals.

The manifold alternation of plates of gypsum and tuff is not less important. This is shown in the accompanying diagram from Hoffmann's paper of a profile view in the Valle di Muria, in Lipari.



*a*, a thick bed of lava;

*b*, pale red tuff-beds, about an inch thick, in which the gypsum plates are about half an inch thick.

Both beds alternate some hundred times, and are intersected by irregularly branched thick veins of fibrous gypsum.

This profile shows, unmistakeably, that the formation of gypsum commenced above, where the condensed vapours, the sulphuretted hydrogen of which was oxidized by the air, have penetrated, and that the water percolating through the beds has carried the sulphate of lime into the irregular veins. Such a phenomenon suggests to us the probability that other analogous deposits have originated from similar reactions, although we may not be able to trace them so well.

The veins of carbonate of lime in the melaphyr, near Niederkirchen, Rhenish Bavaria,\* present tolerable geognostic analogies with the gypsum deposits in Lipari, ramifying like these throughout the surrounding rock, and the only difference being that they

\* Leonhard, *Jahrbuch der Min.*, &c., 1837, p. 641.

reach into the principal fissures. This carbonate of lime has not risen from below, any more than the gypsum in Lipari. The carbonic acid of the atmosphere has converted the silicate of lime of the melaphyr into carbonate of lime, just as in Lipari the oxidized sulphuretted hydrogen has converted the lime of the tuff into sulphate, and both substances have been carried into the fissures by water and there deposited.

If it is remembered that volcanic activity is connected with the formation of gypsum only in so far as it generally, or at least very frequently, terminates in exhalations of sulphuretted hydrogen, it will be evident that the same formation of gypsum may take place even where there are no traces of former volcanic action, but only exhalations of sulphuretted hydrogen originating from processes similar to those going on in the solfataras, but unconnected with that action. The conditions for the formation of sulphuretted hydrogen exist in most sedimentary strata in the same degree as in the solfataras.

Other sulphates, besides gypsum, are formed in the solfataras. At that of Puzzuoli, there has long been an alum and sulphur factory. In the main crater of the island Vulcano, numerous altered rocks are met with, which have been decomposed throughout by the vapours, and have still retained their solidity. Crusts of green vitriol and alum-stones are there common phenomena.

In the crater of Teneriffe, which is a solfatara, the vapours convert the trachyt into white clay, probably also into alum-stone, and sulphur is deposited in drusy cavities, in beautiful crystals, under the softened and detached scales.\*

In attempting to account for the origin of the carbonaceous substances formed, and still being formed, by the sulphuretted fumaroles of the Lipari islands, we must take into account the organic remains in the marine sediment, which was covered by volcanic matter at the time of the elevation of these islands. The immense evolution of sulphuretted hydrogen accompanying the elevation of the new island upon the south coast of Sicily, in the year 1831, suffices to show what happens when volcanic masses burst through the bottom of the sea. There is good reason for regarding the gypsum in sea-water as being chiefly, if not exclusively, the sulphate which is decomposed by organic remains. If sea-water constantly penetrates into the focus of a solfatara, the materials for the evolution of sulphuretted hydrogen are always

\* Leop. v. Buch, *Physikal. Beschreibung der canarischen Inseln*, 1825, p. 232.



renewed. Lastly, the fuci show that marine plants are capable of yielding, independently of the sulphates, in sea-water, enormous quantities of sulphuretted hydrogen (p. 311, note). Still, even the sulphates they contain are derived from sea-water. We have good grounds for ascribing the chloride of ammonium sublimed from volcanos near the sea, to the organic substances carried to their foci by sea-water (p. 212); and it is indisputably these substances which, in contact with sulphates, give rise to the formation of sulphuretted hydrogen.

The numerous examples of such exhalations, described by L. von Buch,\* prove that the conditions requisite for these exhalations are by no means merely local, but exist in innumerable islands. The new Kameni, elevated in the Greek Archipelago from 1707 to 1709, still continues to evolve sulphuretted hydrogen. In the island of Milo (Chap. I, No. 2) these exhalations bleach and decompose the trachytic rock.† Upon the 31st of January, 1811, a violent earthquake took place at the western end of the island St. Michael: the ground was fissured, and a very strong odour of sulphuretted hydrogen was perceived. Phenomena similar to those which presented themselves on the south coast of Sicily‡ are everywhere met with.

Sainte-Claire-Deville§ recently examined the alterations which the rocks, in the environs of the solfataras upon Guadaloupe, had undergone from the action of the vapours impregnated with sulphuretted hydrogen. The following are the results:—

	Unaltered Rock.	Altered Rock.	
		Dried.	Hydrous.
Silica ....	57·95	62·71	50·79
Alumina .....	15·45	27·59	22·32
Protoxide of iron and manganese ....	1·45	....	....
Peroxide of iron .....	9·45	6·29	5·10
Lime .....	8·30	3·02	2·42
Magnesia .....	2·35	0·20	0·17
Potash .....	0·56	0·71	0·55
Soda ....	3·03		
Water .....	....	....	18·98
	98·54	100·52	100·33

\* Poggend. Annal. Vol. 10. Compare my paper, loc. cit., p. 233, &c.

† It certainly cannot be doubted that the decompositions described as occurring at this place are solely the result of the action of sulphuretted hydrogen.

‡ Poggend. Annal. Vol. 24, p. 74.

§ Comptes rendus. Vol. 35, p. 261.

The altered rock was not in the last state of decomposition, in which it forms a plastic clay, still containing protoxide of iron. The results of these analyses show that by the action of vapours, the alkalies and the magnesia were nearly removed, the quantities of lime and iron were diminished, while those of silica and alumina were increased. Concretions of gypsum, alum, and silica, are frequently found in cavities of the rock, and the water issuing from these cavities contains sulphuret of sodium and protoxide of iron. The fumaroles, the temperature of which is  $203^{\circ}$  to  $205^{\circ}$  F., chiefly consist of aqueous vapours; they deposit sulphur in fissures and clefts, where the smell of sulphuretted hydrogen is frequently recognised.

Upon passing 100 litres of aqueous vapour, mixed with sulphuretted hydrogen and air, during a period of many months, through a tube filled with 19 grammes of this rock, Deville found the residue porous, soft, penetrated with sulphur, and containing 17% alumina. The condensed aqueous vapour contained some sulphur, 0.323 grains sulphuric acid, 0.126 lime, and 0.038 peroxide of iron. This experiment shows that silicates are decomposed by continued action of aqueous vapour at  $212^{\circ}$  F., sulphuretted hydrogen and air; alkalies, earths, and metallic oxides being carried away.\*

Sulphurous acid occurs naturally only as a product of volcanic action. H. Davy† found it in the smoke of Vesuvius, in May, 1814, and on the 5th December, 1819, in such quantity that he was compelled to keep at a distance. Monticelli and Covelli‡ found that the only free acid in the smoke on the 28th February, 1822, was sulphurous acid, which was continually produced in the fissures and holes when atmospheric air was in contact with the red-hot lava.

It is quite impossible to imagine that sulphur exists in a free state in lava; it can only be in combination with the metals of the alkalies or earths, or with iron. When sulphuret of potassium is prepared by igniting sulphate of potash and charcoal-powder, the

\* Since Deville holds it as not yet ascertained that all sulphurets in springs are produced by the decomposition of sulphates, I must suppose that he is not acquainted with my investigations, made long ago. The nature of the decomposition of silicates by carbonic acid, which he ascribes to the researches of Fournet and Ebelmen, was already ascertained by myself 27 years ago (*Das Gebirge in Rheinland—Westphalen von Nöggerath*. 1826. Vol. 4, pp. 250 et seq.; and *Die vulkanischen Mineralquellen*, 1826, p. 298, et seq.), consequently, long before the communications of these naturalists were published.

† *Annal. de Chim. et de Phys.*, Vol. 38, p. 133.

‡ *Loc. cit.*, Vol. 1, p. 34 and 58.

smell of sulphurous acid may be distinctly recognised as long as the mass in contact with the air is fluid or red-hot, a part of the sulphur of the sulphuret of potassium being oxidized by the atmospheric air. When, on the contrary, the mass has cooled, and is in contact with moist air, it evolves an odour of sulphuretted hydrogen; the water of the atmosphere and the sulphuret being mutually decomposed in consequence of the presence of carbonic acid. The flakes of scoriæ, carried by the wind to the Sicilian coast, from the island thrown up in the Mediterranean, were observed by Hoffmann\* to smell, not of sulphurous acid, when broken while fresh, but of sulphuretted hydrogen, for they had become cooled while floating on the water. In the smoke of the solfatara of Puzzuoli, also, Monticelli and Covelli were unable to detect any sulphurous acid.

There is very little to justify the assumption of any other processes in the volcanic foci by which this acid is formed. According to all that is yet known of the exhalation of this gas, its formation pre-supposes the presence of atmospheric air, and it can therefore only be supposed to take place at such depths as the air has access to, whether the sulphur is furnished by a metallic sulphuret or by sulphuretted hydrogen. The occurrence of sulphurous acid in connection with volcanic action, is not at all a rare phenomenon in the Italian solfataras; the grottoes at Santa-Fiora, in Sienna, Ætna, the volcanic islands of Stromboli, Bourbon, the volcanos in Java and the Andes, &c., offer many examples. It also occurs in the water of springs near active volcanos.

Many excellent examples are known of the occurrence of sulphuric acid in the craters of volcanos; for instance, the Pusambio river or Rio Vinagre, which flows from the Purace in the Andes of Popayan,† and the sulphuric acid lake in the interior of a solfatara upon Mount Idjen, in the province Banga-wangie, upon the eastern side of Java, from which also a river flows. There is no doubt that in both instances the acid originates from sulphuretted hydrogen. Thus Humboldt found in the fissures in the lower lagune at the summit of Purace, water containing sulphuretted hydrogen, and at their opening a crust of sulphur. Even the water of these lagunes is covered with a film of sulphur. The water of the sulphuric acid lake in Java is, according to Reinwardt,‡ white

\* Poggend. Annal. Vol. 24, p. 74.

† Humboldt, Annal. de Chim. et de Phys. Vol. 27, p. 113, et seq.

‡ Boon Mesch, Disputatio geologica de incendiis montium igni ardentium insulæ Javæ, &c. Ludg. Bat. 1826.

(owing to precipitated sulphur), and vapour of sulphuretted hydrogen escapes from it; the crater contains immense masses of sulphur,\* many openings are especially incrustated with it. Reinwardt mentions many other sulphuric acid lakes in Java, as those in the crater of Patuha, and upon the Talaga Bodas, where large quantities of deposited sulphur are likewise found. All these circumstances indicate that it is only from exhalations of sulphuretted hydrogen that sulphur originates; a part of it separates, while a part is converted into sulphuric acid without any intermediate oxidation to sulphurous acid. This is probably also the case with regard to the sulphuric acid in the Zoccolino-grotto in Tuscany, according to Baldassani; at a grotto in Milo, according to Tournefort; and in a cave on *Ætna*, according to Dolomieu. The sulphuric acid which is found in volcanos has not, therefore, been formed in their foci, any more than sulphurous acid, but has, like it, been formed at the surface, or at places to which atmospheric air had access.

Sulphur cannot exist at a high temperature, together with most of the oxides which, as far as we are acquainted with it, constitute the surface of the earth, without entering into combination with their metals; consequently, assuming that the earth was formerly in a state of igneous fusion, uncombined sulphur cannot be supposed to have existed in it. However, we will not attempt to seek in a mere hypothesis for evidence against the existence of primitively uncombined sulphur; but no one could doubt that a volatile substance like sulphur would, even at the present day, sublime from the interior of the earth, where there is undoubtedly a higher temperature than at the surface. The products of sublimation would be found most abundantly in fissures reaching to depths at which there is a temperature sufficient to cause their volatilization, especially in the craters of volcanos. But sulphur is very rarely met with in fissures, and when it is, only as a product of decomposition. In volcanos, indeed, it is frequent, but likewise only as a secondary product; for it is impossible to imagine its existence in contact with oxides at the volcanic focus. A direct sublimation in the craters of volcanos is only possible when it occurs in combinations, such as sulphurets, which lose a part of their sulphur by heat, or when during an eruption, the sulphur formerly deposited by fumaroles, is volatilized by the increased heat.

\* Gilbert's Annal. Vol. 73, p. 156.



It has already been shown that sulphur may separate from sulphuretted hydrogen, and 21 years since I pointed out the very frequent occurrence of sulphur in sulphuretted springs.\* The waters of Baden, Eilsen, Aix, and Euganeæ, &c., are examples of this fact.

Breislak† very correctly regards sulphuretted hydrogen as playing the principal part in the formation of gypsum and the deposition of sulphur. Thus he found‡ a quantity of sulphur as a deposit from the sulphuretted waters below Pujo, at Garigliano, at Sanno, and at Castel á Mare, on the walls of fissures in the solfataras of Puzzuoli, from which the heated sulphuretted hydrogen escapes; and where it mixes with the air, he observed small drops of water which contained small yellow particles, which gradually increased in size with the drops, and were nothing less than sulphur. In the crater of the solfataras, by making the sulphuretted hydrogen circulate in tubes, he constructed an artificial fountain which yielded daily more than 3,000 pints of water, and the interior surfaces of the tubes were, after some time, coated with crystals of sulphur.

The deposit of sulphur in the Kaiserquelle at Aix-la-Chapelle likewise shows that such deposits result from the decomposition of sulphuretted hydrogen. I found some gypsum, and an organic substance, mixed with this sulphur;§ the latter had separated with the sulphur from the vapours, and the gypsum undoubtedly resulted from the partial oxidation of sulphur, and subsequent action of the acid upon the carbonate of lime of the spring water, or upon the marble with which the well is lined; at least, this marble is so decomposed by the gas and vapours that pasty masses may be removed by the hands. The deposition of this sulphur shows that even very minute quantities of sulphuretted hydrogen are sufficient to cause this; for, according to Monheim, the quantity of this gas in the water of the Kaiserquelle amounts to only 0·5 per cent. of its volume.

The separation of sulphur from sulphuretted hydrogen takes place in the sulphuretted springs themselves. So long as the water does not come in contact with the air, it remains perfectly clear, but, under the influence of air, it becomes milky, in conse-

\* Schweigger's Journ. Vol. 66, p. 123.

† Loc. cit. Vol. 2, p. 262.

‡ Topographia Physica della Campania, etc. Firenze, 1798. An abstract by L. v. Buch, in Gilb. Annal. Vol. 5, p. 398.

§ According to Vauquelin (Schweigger's Journ., Vol. 41, p. 121), native sulphur generally contains some bitumen.

quence of the separation of sulphur. The lakes in the solfataras present the same phenomena: sulphur deposits are formed in this way at Lubin, near Lemberg;\* the water there is strongly impregnated with sulphuretted hydrogen, and where it cannot flow rapidly away, forms a morass, surrounded by turfy soil. A quantity of sulphur, amounting to 25 tons weight, has accumulated there. At Sklo, west of Lemberg, at Mikulince, in Podolia, and several other places, sulphur springs are found in great numbers. It is beyond all doubt that all the sulphur which is deposited by the water of these springs originates from decomposed gypsum; for, upon sinking small pits through the vegetable mould in the neighbourhood of Lubin, Walcher found this substance in a corroded and drusy state, and containing in cavities grey sulphur, such as the springs throw out. The grey lamellar gypsum gave out a very offensive odour when rubbed.

It is very probable that the sulphur which occurs in tertiary coal, as at Artern, Frielendorf, near Ziegenhain,† at Kommotau, in Bohemia,‡ at the Radoboj works in Croatia,§ &c., as well as that occurring in quartz sand of the tertiary coal at Roisdorf, near Bonn, has originated in a similar manner.

The simultaneous formation of gypsum and separation of sulphur may be effected artificially by bringing sulphuretted hydrogen in contact with moist chalk. When this gas is heated up to 212° F. sulphur is deposited in the conducting tube, where it comes in contact with the air;|| it may, therefore, be readily understood that moderately heated sulphuretted hydrogen continually streaming into a bed of limestone, may give rise to the formation of gypsum and the deposition of sulphur, when atmospheric air is not excluded.

While, on the one hand, sulphur is separated from gypsum which is saturated with bituminous substances, by a simple decomposition, sulphuretted hydrogen streaming through beds of limestone, gives rise to the simultaneous production of gypsum and sulphur, the very frequent association of these two substances admits of no other explanation.

We are indebted to Fr. Hoffmann¶ for very interesting descrip-

\* Walcher, in v. Moll's *Jahrb. der Berg. und Hüttenkunde*. Vol. 4. p. 195, et seq.

† Strielpmann and Bunsen, in the *Jahrb. für Mineral*. 1843, p. 809.

‡ Marx found some perfectly developed crystals of sulphur in the tertiary coal of Helmstädt. *Erdmann's Journ.* 1837. Vol. 10, p. 53.

§ *Jahrb. f. Mineral*. 1845, p. 237.

|| Memoir of the author, *Jahrb., für Chemie*. Vol. 66., p. 147.

¶ *Karsten's and v. Dechen's Archiv., &c.* Vol. 13.

tions of the deposits of sulphur in Sicily. Adrian Paillette\* has subsequently written upon them, without however adding anything essentially new. In an island, where volcanic action has gone on since the most ancient period, and still continues upon a gigantic scale, it might be conjectured that the enormous beds of sulphur there, originated from sulphuretted hydrogen, exhaled from solfataras. However, although all circumstances lead to the opinion that all the sulphur has been separated from sulphuretted hydrogen, this gas has not escaped from true solfataras. In the neighbourhood of Sciacca there are still an extraordinary number of sulphuretted springs whose temperature rises as high as 133° F.

According to Hoffmann, the sulphur in Sicily occurs near large masses of gypsum, and generally alternating with limestone, marl, and clay, which are not so extensive as the gypsum. All the known deposits of rock-salt there are associated with sulphur at their northern boundary, as well as with the minerals which are always found together with rock-salt, gypsum, and clay. The sulphur is situated partly in holes in corroded limestone, where it frequently forms small druses,† incrustations, and nodules an inch thick, and is partly disseminated in veins.‡ It is very irregularly distributed, and perhaps always more abundant near the larger fissures; incrustations and druses of calcspar always occur together with it. In some sulphur druses there are strontianite, and rarely gypsum crystals, which are also formed in the limestone druses.

Bituminous gypsum and aqueous vapour are evidently the materials from which this sulphur is produced, and since the former as accompanying rock-salt is undoubtedly a marine deposit, we must regard sea-water as the source of the immense quantities of sulphur in Sicily. Even if the aqueous vapour has a temperature of only 111° F., it is capable of disengaging sulphuretted hydrogen from sulphuret of calcium. Hoffmann found, however, in the sulphur mine of Solfara Grande a temperature of 95° F., which is not far short of it.§ The occurrence of sulphur is always con-

\* Comptes rendus, 1843. No. 18. Paillette does not show any great acquaintance with long-known facts. His theory, which, in the report upon his paper, is called ingenious, I had put forward myself fourteen years before. Loc. cit., p. 144, &c.

† The qualitative analysis of a specimen of limestone, containing a very fine druse of large crystals of sulphur, proved it to contain but very little carbonate of magnesia, but rather more sulphate of lime.

‡ The veins of sulphur in gneiss and granite at Tetenti, near St. Giorgio, east of Capo Calava, have very probably been formed in the same way.

§ There is, however, nothing inconsistent with the assumption that, in Sicily and other places where sulphur occurs, hot aqueous vapour has risen from

nected with an uncommonly high temperature, and it is on this account that the sulphur druses are only found at a tolerable depth below the surface. Drops of water are everywhere found hanging upon the small sulphur stalactites. There is likewise no doubt that it was aqueous vapour which has rendered the limestone so full of holes, and deposited the dissolved carbonate of lime in the form of calcspar, for it was mixed with the carbonic acid formed by the decomposition of organic remains.

The aqueous vapour which still deposits sulphur in the sulphur mines of Sicily, can contain but a very little sulphuretted hydrogen; for Hoffmann does not make any mention of having experienced a difficulty in breathing, or any other unpleasant symptoms, when visiting these mines. Hoffmann's observation that the gypsum is sometimes altogether wanting, while in the mine Cara Pape it is associated with sulphur, in crystals one or two feet long, shows that the circumstances under which sulphur was separated from sulphuretted hydrogen, and sulphuric acid and gypsum were formed, must have been very different. But even these gypsum crystals may only have been derived from the beds of gypsum forming the roof of these mines, and from whence the sulphate of lime may have been washed downwards by water. It is quite certain that no sulphuric acid has been formed where the sulphur is incrustated or associated with calcspar, but that all the sulphuretted hydrogen has been converted into sulphur and water. As this decomposition requires much less oxygen than the formation of sulphuric acid, it is evident that where the access of atmospheric air to the porous limestone was limited, the former change alone could take place. If, now, only a part of the sulphuretted hydrogen in the interstices of this rock was converted into sulphur and water, while the remainder escaped to points nearer the surface, where the air had more ready access, it was then completely oxidized.

The connection between the volcanic phenomena in Sicily, Iceland, &c., and the occurrence of sulphur, consists in the fact, that wherever there is volcanic action, there is a high temperature at a shorter distance below the surface than is otherwise the case, and also because volcanic eruptions cause a rending of the strata for a considerable distance round and to a great depth. The temperature of a bed of bituminous gypsum at a moderate depth may thus be raised so high as greatly to facilitate its conversion into

great depths to near the surface, there penetrating beds of bituminous gypsum, and causing the separation of sulphur.



sulphuret of calcium, and by the action of hot water into sulphuretted hydrogen. The rending of the rocks in the neighbourhood of volcanos renders the occurrence of ascending springs possible, the waters of which likewise communicate a high temperature to the strata near the surface. Lastly, we must not forget that the exhalations of carbonic acid, frequently so abundant in volcanic districts, may, when they pass through beds of decomposing gypsum, cause the evolution of sulphuretted hydrogen from sulphuret of calcium.

Paillette directs attention to the fact, that the constant association of sulphur with rock-salt may also be observed in Spain, the Pyrenees, in northern Europe, and, indeed, everywhere in the upper strata of the chalk-formation. According to Delesse,\* a bituminous clay-formation occurs near Cracow, containing sulphur and rock-salt, together with fossils belonging to the chalk and tertiary formations. Al. Brongniart, Elie de Beaumont, and Dufrenoy, in their report upon his paper add, that the sulphur does not occur only in the positions mentioned by him, but is rarely and perhaps never confined to one formation. The bed at Teruel, in Arragon, in which, according to Braun†, there are myriads of planorbis and chara converted into sulphur, clearly shows that this substance has been produced since the deposition of the freshwater tertiary beds.

The sulphur occurring in druses of trachyte, mica schist, lava, sandstone, in hollows of flint pebbles, &c., has certainly no other origin than exhalations of sulphuretted hydrogen which have passed through these rocks. On the contrary, the sulphur in veins containing metallic sulphurets has originated otherwise. When associated with galena and carbonate of lead, the mode of its production cannot be doubtful. The carbonate of lead has been formed by the decomposition of galena, as is evidently shown by the pseudomorphs of this substance in the form of galena. The sulphur found near it can therefore only be derived from galena which has suffered decomposition. The sulphur which is found at Tarnowitz, in Silesia, associated with oxide of lead, has likewise the same origin, since this latter substance is a product of the decomposition of carbonate of lead, produced by that of galena. The sulphur occurring together with other metallic sulphurets, such as copper pyrites, or iron pyrites, is undoubtedly derived from the decomposition of these minerals. The sulphur found as a sublimate,

\* Journ. d'un voyage en Pologne.

† Bull. de la Soc. Géol. de France. Vol. 12, p. 169.

where beds of bituminous coal are burning, and which occurs even in fine crystals, probably originates from the decomposition of pyrites by heat.

When all these facts are considered, we cannot but come to the conclusion that sulphur is in no case a primitive production, but, as far as regards its principal localities, has resulted from the decomposition of sulphuretted hydrogen.

Like carbon, sulphur appears to owe its existence in a free state to the organic kingdom. Carbonic acid is decomposed by living plants; sulphates are decomposed by dead organic matter. In this instance, as in so many others, the important influence of the organic kingdom upon the inorganic is perceptible, and the existence of sulphur prior to organic life appears very doubtful.

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## CHAPTER XVII.

### CHLORIDES, BROMIDES, AND IODIDES.

IT is very rare to meet with a mineral or fresh water, which does not contain traces at least of chlorides, in most cases chloride of sodium. Among 38 fresh-water springs examined by me, which proceed out of felspathic porphyry, granite, syenite, trachyte, dolerite, and basalt, there was not one, the water of which was not rendered turbid by nitrate of silver. In most of them, the presence of chlorides of calcium, magnesium, and sodium, could be detected.\* Of all easily soluble salts, this is the most abundant. As rock-salt it frequently forms layers of great thickness. In sedimentary formations also, which contain no rock-salt, there are almost invariably present traces at least of chloride of sodium. Its almost never-failing presence in springs need not then be a matter of surprise. In springs which proceed from crystalline rocks it is also present; in regard to such springs, however, it cannot be maintained that in every case they arise in the rocks themselves, and not in the adjacent sedimentary formations.† The presence of chlorides in crystalline rocks is not only indicated by

\* German Edition. Vol. I, p. 547, et seq.

† Ibid, Vol. I., p. 457, et seq.

the circumstance that springs proceeding from such sources contain these salts, but has also been proved by direct examination.

Among the volcanic rocks containing chlorine, or hydrochloric acid, the following may be noticed:—In pumice-stone,\* as well as in lavas from Vesuvius, *Ætna*, *Stromboli*, and from the islands of *Lipari* and *Vulcano*, hydrochloric acid was detected by *Spallanzani*.† The surface of the lava which issued from *Vesuvius* in 1794, was a few days after the eruption covered with beautiful crystals of chloride of sodium and chloride of ammonium. The clefts in the crater of *Vesuvius* were found by *von Buch*, after the eruption in 1805, to be thickly covered with white salt, which was determined by *Gay-Lussac* to be almost pure chloride of sodium. *Monticelli* and *Covelli*‡ found in the lava which flowed from *Vesuvius* in 1822, 0·09% of chloride of sodium, and in the slags which covered the glowing lava they frequently found very beautiful crystals of the same salt. In general, according to these authors, chloride of sodium is the most prevalent salt in all the products of the eruptions of this volcano. In *puzzolane* from *Vesuvius*, *Stengel* and *Reinhardt* found from 2·56 to 3·25% of chloride of sodium, and in volcanic bombs from the same volcano the latter found 1·60% of this salt.§ In the year 1827, two newly formed craters in this volcano deposited large stalactites of salt.|| The masses of salt which were thrown out by *Vesuvius* in 1822 were so large that the inhabitants of the neighbouring villages collected them for domestic purposes, until the government officers claimed them as a perquisite of the crown. They consisted of two different kinds of substance, the one beautifully crystallised, white, and pure, the other of a red colour and much harder.

After some of the eruptions of *Mount Hecla*, salt was found in such quantity as to be more than sufficient to load several horses.¶ *Berth* observed different parts of the surface of the lava which was thrown out by the volcano in the island of *Bourbon* in 1791, but especially the fissures which existed in it, to be covered with crystallised chloride of sodium.

\* According to *C. Gmelin* (*Gilbert's Annal.*, Vol. 64, p. 370), a very acid fluid, containing hydrochloric acid, is evolved from pumice-stone when it is heated in the flame of a spirit-lamp.

† *Breislak Lehrbuch der Geologie*. Vol. 3, pp. 57 and 94.

‡ *Vesuvius*. German translation, p. 191.

§ *Journ. für prakt. Chemie*. Vol. 34, pp. 438 and 441.

|| *Donati im Jahrb. für Mineralogie, &c.*, 1833, p. 577.

¶ *Olafen und Povelsen Reise durch Island*. Kopenhagen, 1774. Vol. 2, p. 136.

The origin of this substance in the products of volcanic eruptions will be considered in the following chapter.

In a porous rock which forms a large part of the Puy-de-Sarcouy, in the mountain chain of the Puy-de-Dome, Vauquelin found 0.055% of hydrochloric acid.\* In basalt Kennedy found 0.01% of the same acid, Klaproth 0.001, and myself 0.00085%. In trachyte conglomerates from the Siebengebirge, in a salt yielded as an efflorescence by the slag of the Falkenlei, near Bertrich, and in one yielded very abundantly by the trass rocks in the valley of Brohl, I also found chlorine. If the chlorine contained in these was combined with sodium as chloride of sodium, this salt must have amounted to 14.3%. In trass itself, taken from a quarry, I found chlorine in considerable quantity. In the lava of Niedermendig, Kersten found a small quantity of chloride of sodium.

According to Abich,† the trachyte of the Drachenfels contains 0.45% of water, chlorine, &c.; the lava of Monte Nuovo, 0.68% of chlorine; the Piperno of Pianura, 0.15% of chlorine; the lava of the Arso, on Ischia, 0.56% of water and chlorine; the rock from the summit of Chimborazzo, 0.41% of chlorine (and loss by combustion). In like manner, according to him, obsidians and pumice-stones contain chlorine; that in the pumice-stone of the island of Pantellaria amounting to 0.7%. In the trachytic tufa of the Campi Flegraei, and of Pausilippo, there are present traces of sal-ammoniac. The same is the case with the basaltic tufa of the island of Vivaria. The rock constituting the circus of the Peak of Tene-riffe, contains 0.3% of chlorine.

Most of the examinations which have been made of rocks, with a view to ascertain the quantity of chloride of sodium existing in them, we owe to the exertions of the deceased Struve.‡ In all the specimens of Bohemian basalt, phonolite, &c., examined by him, as well as in a twin crystal of felspar from the granite of Carlsbad, he found small portions of hydrochloric and sulphuric acids. On treating these rocks with carbonated water, under a pressure of  $1\frac{1}{2}$  atmospheres, he effected a (partial) decomposition of the silicates of soda and potash contained in them. In this way he succeeded in extracting from three different specimens of basalt, three of phonolite, from felspathic porphyry; from gneiss, granite, and from clay-slate, quantities of chloride of sodium more or less

\* *Annal. du Museum.* Vol. 6, p. 98.

† *Geolog. Beobachtungen über die vulkanischen Erscheinungen in Unter- und Mittel-Italien.* 1841.

‡ *Ueb. die Nachbildung der natürlichen Heilquellen.* Heft. 2, p. 17, fol.



observable, besides other salts. In the extract from granite and clay-slate he found, in addition to chloride of sodium, chloride of potassium, and in gneiss chloride of potassium, but not chloride of sodium.

The presence of chloride of sodium in crystalline rocks is indicated by the efflorescence of this salt which forms upon them. Such an efflorescence is observed upon gneiss in the hill of Gohier, below Nantes.

The granite which was treated by Struve with carbonated water, and yielded chlorides of sodium and potassium, was from Carlsbad. The hot springs of that place may not, however, derive their chloride of sodium from the granite, but may convey it into this rock, as it is probable the formation of the mineral water goes on at some other quarter. It is sufficient to be aware of the possibility that the salt in question may proceed from the granite. By treating the phonolite of Bilin with carbonated water, under a pressure of nearly three atmospheres, Struve\* obtained a water very like that of the acidulous springs which exist there, and by treating in a similar manner porphyry from the foot of the Schlossberg at Teplitz, he also obtained one similar to that of the Steinbad at that place. It cannot be doubted then that the chloride of sodium in both these mineral waters is derived from these rocks. In the porphyry of Kreuznach, E. Schweizer† found chloride of sodium, as well as chlorides of potassium, calcium, and magnesium, which could be extracted by water without the addition of carbonic acid. The quantitative determination of the chlorine gave 0.1%. In the neighbourhood, and also from the porphyry, there rise saline springs; the place, however, from which the specimen submitted to analysis was taken is a considerable distance from these. In the melaphyre which is present in the Keuper and Muschelkalk, in Franconia, v. Bibra‡ found 1% of chloride of sodium.

The circumstance that chlorides may be extracted from crystalline rocks in the way above mentioned, must indicate the presence of the former in the minerals of which the latter are composed. In many minerals also chlorine is found, as in lithia mica, apatite, eudialyte, pyrosmalite, sodalite, in hornblende, cläolite, nepheline, ittnerite, antrimolite, erenite, nosean, hauyne, lapis-lazuri, davyne, bautite, &c. The quantity of the chlorine in sodalite amounts to 6.75%.

\* Loc. cit., p. 47.

† Poggendorff's Annal. Vol. 51, p. 287.

‡ Journ. für pract. Chemie. Vol. 26, p. 29.

Only in a few cases has it been shown that the chlorine is combined with sodium. According to Scheerer,\* that contained in eläolite and nepheline cannot be expelled by heat until a very high temperature is attained; hence, then, it does not seem to be present as chloride of magnesium. Since, also, it cannot be removed by treating the mineral, reduced to fine powder, with water at a boiling temperature, he concludes that it forms a true mineral combination, replacing perhaps a small quantity of silicic acid. On the other hand, however, it appears that no chlorine can be extracted from sodalite also, although in that mineral it is undoubtedly present as chloride of sodium.

By exhaustion with water, Struve† obtained chloride of magnesium from the Saldschitz-marl, which is probably a mixture of decomposed basalt, quartz-sand, and carbonate of lime, as well as from Püllna-clay, which he supposed to be formed of decomposed basalt and phonolite. We cannot, however, from this conclude that the chloride in question existed in the original basalt and phonolite, inasmuch as its presence in the products of the decomposition of these rocks may have been owing to accidental circumstances, and that it was carried from other places by water.

It is quite the same, so far as regards the process of formation of mineral springs arising in crystalline rocks, whether the chlorine be present in combination with sodium, or with one of the earthy metals (magnesium, calcium). In such mineral waters carbonate of soda is never wanting; consequently, when chlorine has been extracted in combination, not with sodium, but with one of the metals of the alkaline earths, this chloride, which may be chloride of magnesium, is always decomposed into chloride of sodium and carbonate of magnesia. The circumstance that we never meet with any other chloride except that of sodium in the waters in question, does not consequently warrant the conclusion that this is the only chloride which is present in the crystalline rocks.

Since chlorine is present in so small a quantity in crystalline rocks, it is to be expected that bromine and iodine, if they occur here along with that body, must be present in such minute proportions as almost always to escape detection.‡ Since, however,

\* Poggendorff's Annal. Vol. 49, p. 370.

† Loc. cit., p. 28.

‡ Supposing that the bromides and iodides occur in rocks in the same proportion as they are found in springs, these salts may amount to from 1-500th to 1-1500th, and even to still smaller fractions, of the amounts of chlorides. But such minute quantities of bromides and iodides escape detection, inasmuch as the chlorides amount to only 1-1000th or 1-10,000th part of the rock. . .

bromides and iodides have been actually found in the mineral kingdom in quartz dykes and veins, in clay-slate in Mexico, and Huelgoat in Bretagne, and since when bromide and iodide of silver occur, they are always accompanied by chloride of silver, it is not unlikely that the three are associated in these crystalline rocks also.\* This is further indicated by the fact, that in mineral springs containing bromine and iodine, chlorine also is invariably present, and always in much greater quantity than the other two.

In all mineral waters in which chlorides and iodides occur, Cantu† found corresponding bromides likewise. From his further researches, he believes he is warranted in setting it down as a general rule, that wherever chlorides occur, bromides and iodides occur also. The circumstance of iodine having also been detected by him in mineral springs which arise at the foot of the Piedmont Alps, in primary formations, is a matter of interest.‡

The brine springs containing iodine, which occur in the Andes, proceed, according to Boussingault,§ from the oldest rock-formations, as well as from the most recent strata, and are supposed by him to derive their saline ingredients from the crystalline rocks of which these gigantic formations are composed. In the mother-liquor also which remains after the preparation of Carlsbad salt, very small quantities of iodine have been found by Nentwich and Pleischl.||

In mineral waters bromine is commonly found as bromide of magnesium, and iodine as iodide of sodium.

Sigwart¶ found iodine in the sulphuretted springs of Sebas-

\* Whether the iodide of mercury at La Loma del Encinal, in Mexico, be accompanied by a corresponding chloride, is unknown, inasmuch as it occurs not in dykes, but in quartz detritus, which belongs to a conglomerate alternating with aluminous marl, probably of the tertiary series.

It is deserving of mention, as a remarkable circumstance, that in old coins, chiefly in the Grecian and in the Saxon coins of the thirteenth century, but also in those of the Romans, chloride and bromide of silver were found by Brüel (Karsten and v. Dechen's Archiv., Vol. 18, p. 505). It appears that these salts were not originally contained therein, but have been introduced from without. The fact, however, of their being found together in these coins, also goes to show that chlorine and bromine are always associated.

† L'Institut. No. 587. 1845.

‡ It is remarkable that bromine and iodine were also found by Cantu very abundantly in organisms which inhabit running and stagnant waters, even in places removed from the sea. They occur in combination with the same bodies as chlorine, with which latter they appear to be almost invariably associated. L'Institut, No. 611, 1845.

§ Annal. de Chim. et de Phys. Vol. 54, p. 163.

|| Journ. für pract. Chemie. Vol. 5, p. 40.

¶ Württembergische naturwissenschaftliche Jahreshefte. Jahrgang, 19, p. 43.

tianweiler, Boll, and Reutlingen, in Würtemberg; in that of Balingen, even in greater quantity than in brines. Since these springs originate in bituminous slate of the lias-formation, rich in decayed organic remains, he tested this slate, and found this substance in it also.

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## CHAPTER XVIII.

### ROCK-SALT.

THIS substance occurs in all sedimentary rocks from the transition to the tertiary formations,\* and generally associated with gypsum, particularly anhydrite.

Geologists of the first rank in the Plutonic school have regarded the rock-salt present in several localities as masses which have risen from the interior of the earth and found their way into the fissures of previously existing formations. The manner in which it occurs at Bex seemed to favour this view very much. An apparent fissure in anhydrite, from 30 to 40 feet in width, and parallel with strata the direction of which is more or less perpendicular, is filled with coarse fragments and fine particles of the same mineral, together with siliceous limestone. These are all cemented by means of rock-salt into a single, very firm mass, in which no druses are present. The salt is often of great purity and transparency, and is perfectly anhydrous. During the evaporation of its solution scarcely any mother-liquor is obtained from it. In this case it is maintained that the salt could only have been formed by a sublimation of its elements, chlorine and sodium.†

As occurring in the place just mentioned, it is termed by v. Charpentier a layer, or more properly a dyke of rock-salt. It may be asked, however, what reasons there are to controvert the opinion that at one time it lay horizontally like the other strata of the rock, and was afterwards raised into a vertical position together with these. The solid nature of the whole mass, as well as the absence of drusic cavities, might be explained as having been occasioned by the pressure exerted upon it while being raised. The great purity and transparency of the salt affords no better proof of its having

\* Russia affords excellent examples of the truth of the remark, that rock-salt occurs in beds of all ages. Murchison, &c., *Geology of Russia*, Vol. 1, p. 145.

† Von Charpentier, in *Poggendorff's Annal.*, Vol. 3, p. 75.



been formed by sublimation; all rock-salt being, as we shall see, very pure.

As regards the anhydrous condition of the rock-salt of Bex, it is well known that most rock-salt, though undoubtedly formed in the moist way, does not decrepitate when heated, and consequently contains no mechanically inclosed water. Along with the removal of the mother-liquor by the pressure of the upturned strata, the water contained in its interstices has also been expressed.

Regarding the supposed sublimation of the rock-salt, we would direct attention on the other side to the following remarks. During the process of sublimation as it takes place in our laboratories, the temperature of the vessel in which the sublimate is collected is gradually raised by the heat evolved from the gaseous body while condensing. This is to a certain extent counteracted by the surrounding cool air which is constantly being renewed. In a fissure in a mountain, however, surrounded on all sides by imperfect conductors of heat, no appreciable diminution of temperature can in this way take place. On the contrary, the temperature of the neighbouring rock itself must be gradually raised to the same point as that of the body which is being sublimed. The temperature at which chloride of sodium sublimes is very high. The furnaces in which earthenware is glazed by means of chloride of sodium, must be raised to a white heat in order to sublime it. What is the result? The clay of the earthenware and the chloride of sodium are decomposed, the surface becomes glazed while hydrochloric acid and chloride of iron are volatilised.

Must not the same thing have occurred at Bex? The immense quantity of the chloride of sodium sublimed must have caused the walls of the fissure, as well as the fragments of anhydrite present in it, to be heated to the temperature of sublimation. Such is the temperature of the furnaces just mentioned. The walls of the fissure, as well as the fragments of anhydrite which it contains, particularly the siliceous limestone, would have exhibited a glaze upon their surface. On the higher parts of the rocks we should have observed marks of decomposition from the hydrochloric acid evolved, and also sublimates of chloride of iron. Of all this, however, no mention is made by v. Charpentier. The supposition that the chloride of sodium in this so-called fissure has been deposited by a process of sublimation, is therefore an untenable hypothesis.

In like manner we must regard it as doubtful whether the almost pure chloride of sodium with which v. Buch and Gay-

Lussac\* found the fissures thickly covered in the crater of Vesuvius in 1805, and from which hot vapours ascended, was actually sublimed as such.

Exhalations of hydrochloric acid gas take place from Vesuvius. According to Monticelli and Covelli,† this gas was evolved at all periods of the eruption in October, 1822. It is formed whenever watery vapour finds access to chloride of sodium heated to redness along with sand, or to chloride of magnesium only moderately heated. These salts are contained in sea-water, and may consequently easily pass in large quantities along with it into the volcano. The lava contains silicates of potash and soda, which when acted upon by hydrochloric acid are converted into chlorides of potassium and sodium, these making their appearance at the surface in the form of efflorescences. Whether the salt examined by Gay-Lussac was free from chloride of potassium, is not known. The salt thrown out in large quantity by Vesuvius in 1822, as well as that which was found upon the surface of the lava of the eruption of 5th February, 1850, were examined, the former (I) by Laugier,‡ the latter (II) by me. Scacchi§ found in Vesuvius amongst the formations of the gaseous exhalations of 1850, a salt presenting the composition III, and the following are the results of the analyses:—

	I.	II.	III.
Chloride of sodium ...	62.9	46.16	62.45
Chloride of potassium ...	10.5	53.84	37.55
Sulphate of lime ...	0.5	...	
Sulphate of soda ...	1.2	trace	
Silicic acid ...	11.5		
Peroxide of iron ...	4.3		
Alumina ...	3.5		
Lime ...	1.3		
Water and loss ...	3.7		
	99.4	100.00	100.00

Masses which, like these, contain so large an amount of chloride

\* Der Vesuv. Deutsche Uebersetzung, p. 79.

† Ibid., p. 172

‡ Loc. cit., p. 79.

§ Annal. des Mines (4). Vol. 17, p. 323

|| On being dried at a temperature of 212°, this salt, which consisted principally of an uncrystalline mass, lost a large quantity of water. When subsequently

of potassium can proceed neither from sea-water,\* rock-salt, nor from any source of chloride of sodium with which we are acquainted. The salt I, however, might very well have been generated from the decomposition of the lava by vapours of hydrochloric acid. It has certainly not proceeded from the volcano by sublimation, but has rather been hurled forth mechanically in the same manner as the lapilli, ashes, &c. This view is favoured by the circumstance of its being mixed up with substances which are fixed in the fire. Whether the salt II also arose in the same way, we must leave undetermined; the salt III, however, seems to have been formed by exhalations of hydrochloric acid gas.

The hypothesis which attributes the formation of rock-salt to eruptive agency, seemed at one time to be losing ground; but latterly it has been revived with increased assurance.† Nicol found in the rock-salt of Cheshire numerous minute irregular cavities which were filled with a fluid, some of them containing also a small bubble of air.‡ The fluid appeared to be a concentrated

exposed to a red heat, its weight was diminished only 0·13 per cent., a salt, probably sal-ammoniac, being at the same time sublimed. Lime, magnesia, and peroxide of iron, were altogether absent.

\* In sea-water, the chloride of potassium amounts at an average to only one-twentieth of the chloride of sodium.

† C. I. B. Karsten, in his *Archiv.*, Vol. 22, p. 554. Zeuschner (*naturwissenschaftliche Abhandlungen von Haidinger*, Vol. 3, p. 171) supposes that tertiary rock-salt on the northern declivity of the Carpathian chain has been precipitated from the sea; that of the Salzburg Alps, on the other hand, occurs, according to him, as stocks or dykes in the red marble, which have passed from below upwards, and have been accompanied during their ascent by eruptions of mud, consisting of aluminous marl, chloride of sodium, anhydrite, &c. At no time did organic remains occur in these formations, such as are present in those of the Carpathian chain.

The rock-salt of Wieliczka, and that of the Salzburg Alps, are, in a chemical point of view, so identical, and at the same time so different from that thrown out by Vesuvius, as well as from that found upon its lava, that it is certainly a very bold opinion to ascribe a different origin to substances of the same nature, and to regard substances differing from each other as proceeding from like origins. There have never yet been found in rock-salt other constituents than those which are present in sea-water; so far, then, as chemistry is concerned, the opinion that all rock-salt has been formed by deposition from the sea, is liable to no objection. This becomes the more probable, when it is considered that the salt which is really a product of volcanic action is entirely different in composition from that which is merely imagined to proceed from this source. If we would regard saliferous strata as the products of mud eruptions, we might, if we pleased, regard every deposit from rivers in the same light. From such fictions, however, science can derive no benefit. In a secondary formation, no one can expect to meet with the same organic remains as occur in formations belonging to the tertiary series. Organic remains in a rock certainly afford indubitable proofs of its sedimentary origin: to how many rocks, however, must we have been obliged to deny this origin, had we been guided solely by the circumstance of their containing no such remains.

‡ These beds of rock-salt are contained in strata of sandstone and red marl.

solution of chloride of magnesium with some chloride of calcium.\*

In general no organic remains occur in rock-salt. Marcel de Serres and Joly have, however, found in the red rock-salt of Cardona remains of infusoria, to which also they are inclined to ascribe its red or green colour.† Rendschmidt ‡ discovered in the rock-salt of Wieliczka many small brown beetles, and Phillippi found in the same, polythalamia as well as shells. In the saliferous clay of that place remains of conchylia have been long known to exist, and more recently Reuss found in it more than 150 species of polythalamia.§

Infusoria have been found in the saliferous clay of Cardona, as well as in that from the Alps; in the former by Marcel de Serres, in the latter by Schafhäütl.|| It is well known that animalcules occur in brine springs. Murchison¶ found myriads of them in lively agitation in a natural salt pool which was so intensely saline that the body sank in it with difficulty. The bituminous character so frequently presented by rock-salt and saliferous clay seems to depend upon petroleum. Fossil wood has been found in the rock-salt of Ischl, Ilezkaja Saschtschita in Algeria.

Can we then in the face of these facts still ascribe a Plutonic origin to rock-salt? How can it possibly have had such an origin, when, as in the case of saliferous clay, sedimentary formations are blended with it in the most intricate manner?

The so-called crackling salt of Wieliczka, which crepitates on being heated, or when it is dissolved in water, owes this property to the presence of carburetted hydrogen gas in a state of strong compression (p. 254).\*\* Could this gas, then, could the bitumen, or still more, could the organic remains have been preserved in rock-salt had it arisen as an eruptive mass or as a sublimate?††

Lyell, Princip., p. 249. The presence of fluids and of air-bubbles in a formation affords as conclusive evidence of its sedimentary origin, as that afforded by the presence of organic remains.

\* Edin. New Phil. Journal. Vol. 7, p. 111.

† Jahrbuch für Mineralogie, 1841, p. 263; and l'Institut, 1842, p. 267.

‡ Jahrb. f. Min., 1839, p. 630.

§ Ibid., 1843, p. 568; und Sitzungsberichte der Wiener Acad., 1848, Vol. 2, p. 173.

|| Annal. der Chimie und Pharmacie. 1844. Vol. 51, p. 261.

¶ Loc. cit., Vol. 1, p. 185.

\*\* Dumas, in Poggendorff's Annal., Vol. 18, p. 601; and II. Rose, Ibid., Vol. 48, p. 353.

†† We have no difficulty, on the other hand, in conceiving that rock-salt, while crystallising from a watery solution, might take up carburetted hydrogen gas, provided the surrounding medium were filled therewith. This gas is by no means rare in mines of rock-salt, or in brine-pits. The fact of this combustible



No theory seems to harmonise so closely with known facts as that according to which rock-salt is to be regarded as a deposit of the sea. Before bringing forward in further support of this view the results afforded by the analysis of several specimens of rock-salt, we will examine the objections which have been advanced against it in recent times.

Alberti\* supposes that gypsum and rock-salt proceed from water, and that they have penetrated the triassic rocks by elevation, as stock-shaped unmelted masses. In the deeper part of the earth's surface, between its nucleus and crust, there are, according to him, vast spaces which communicate partly with lakes, rivers, and springs, partly with the sea, and are occupied by fluids. From the considerable amount of heat evolved in consequence of chemical combinations and decompositions, as well as during the evaporation and decomposition of water, these fluids have gradually passed into the condition of a syrup, and from this the triassic rocks have derived their gypsum and rock-salt.

Hypotheses which have no other foundation than the imagination of their authors, and which are opposed to chemical and physical laws, form no fit objects for criticism. The present hypothesis, which is quite untenable, we should have left undisturbed, had it not proceeded from a geologist of merit, who, in the capacity of overseer of a salt-work, has had the opportunity of studying very minutely the relations of the bedding in saliferous formations. Alberti† gives profile views of the rock-salt magazines of Ischl and Aussee. In the one, the saliferous clay (Haselgebirge) forms a stock which, so far as its depth has been yet reached, is surrounded by impermeable clay (Lebergebirge) and by limestone. Whether this stock of saliferous clay has arisen by filling from above or below, the space which it occupies must have existed before this took place. Of a syrupy mass, no one can be so unreasonable as to expect that it should break up the limestone rock, and so form a path for itself. Although we can easily understand that an extensive hollow in sedimentary rocks situated upon the bottom of the sea, might gradually become filled up, partly with chemical deposits of rock-salt and gypsum, and partly with mechanical deposits of alumina, we cannot understand how, during the long period which must have been required for the filling up of a cavity which becomes narrower towards the upper part, the

gas being taken up by chloride of sodium while crystallising, may bear some analogy to the absorption of gases by charcoal.

\* Halurgische Geologie, Vol. 2, p. 264.

† Ibid, p. 227

overhanging limestone could have been preserved entire. In the second of the above-mentioned profiles the saliferous clay appears as a bed situated between the limestone layers. Keeping out of view the quite untenable assumption that the saliferous clay was, at a later period, pushed in between the previously existing layers of limestone, the only explanation which seems possible is, that the saliferous clay was deposited subsequently to the deposition of the underlying limestone, while the limestone which forms its roof is a still more lately repeated sedimentary formation.

In opposition to the opinion of Schafhäütl,\* that the dislocation and dispersion of the deposits of salt and gypsum were brought about by a subsequent re-solution of these bodies, especially of the easily soluble chloride of sodium, Alberti mentions that the saliferous clay in the Salzkammergut and at Berchtesgaden is surrounded by impermeable Lebergebirge, and that this saliferous clay since its formation cannot have undergone any change.

In Berchtesgaden and in the Dürrenberg, at Hallein, no water whatever has penetrated the saliferous rocks, it passes only to a little depth; and at Hall in the Tyrol, it has reached the saliferous rocks only through fissures and planes of stratification;† if, therefore, the rock-salt in these localities has been washed away at all, this must have taken place merely to a slight extent. But can it be assumed, with precision, that the relations which at present exist, have remained fixed ever since the formation of the magazines of rock-salt in these places? Elevations and subsidences on a large scale, with the consequent dislocations of strata, have taken place in the Alps. Beds of rock-salt, which were covered by impermeable layers, might consequently, in their original horizontal position, have been quite inaccessible to water, but might afterwards have been exposed to its action, when by their dislocation the impermeable roof was broken in some parts. Even when no alteration of this covering ensued, it might have happened, that between inclined strata a circulation of water took place, which was impossible so long as these retained their horizontal position: such relations are shown very clearly by the subterranean course of springs. If elevations and subsidences took place while the sedimentary rocks were still beneath the surface of the sea, the sea-water would have effected the re-solution

\* *Gelehrter Anzeiger der bairischen Acad. der Wissenschaften* xviii., No. 103, 1844.

† *Germ. edit.*, Vol. I, p. 166.

of the previously deposited rock-salt. This would have happened the more easily if the elevations were rapid, and attended by earthquakes, inasmuch as in this case violent agitations of the sea must have ensued, and water much less or not at all impregnated being brought from places at a distance, the re-resolution of the salt must in this way have been facilitated. More recently, the portions of the saliferous clay which had become exposed to the action of the water, may have been again protected by new mechanical deposits, and thereby the salt which was retained in the rock after its elevation above the level of the sea, and is still present in it, has been preserved.\*

That this removal of the rock-salt in saliferous formations has taken place, and still occurs under the action of water, is shown by the existence of brine-springs, which, when saturated with chloride of sodium, evidently spring from rock-salt. These have and are still extracting large quantities of salt from the saliferous formations, and thus forming excavations, the roofs of which, giving way under the weight of the superincumbent masses, produce dislocations in the overlying strata of rock-salt.

All the occurrences here supposed are possibilities, founded on chemical and physical laws, and with such we must, in the present state of science, be content. Further investigations, particularly those which will be subsequently mentioned in regard to the question of the very highly probable increase of saline constituents in the water of the Mediterranean will, it is hoped, raise the veil a little further.

ANALYSES OF SEVERAL SPECIMENS OF ROCK-SALT.

	I.	II.	III.	IV.	V.
Chloride of sodium....	100.00	99.85	99.928	99.43	98.14
„ of potassium....	....	....†	....	..	trace
„ of calcium....	....	trace	....	0.25	....
„ magnesium....	trace	0.15	0.072	0.12	....
Sulphate of lime....	....	....	....	0.20	1.86
	100.00	100.00	100.000	100.00	100.00

\* The saliferous clay itself might, if the water had extracted the saliferous portions in its upper layers, have afforded material for new formations impermeable by water. This is also seen in the so-called sinking works, where the argillaceous portion of the saliferous clay which forms the roof, after the water has dissolved the saline parts, sink down through the salt-water and form upon the floor an impermeable layer, which prevents the salt water from sinking into the saliferous clay.

† Vogel, however, found in this rock-salt, as well as in that from Hallein and

	VI.	VII.	VIII.	IX.	X.
Chloride of sodium ....	99.63	99.97	98.36	98.81	99.30
„ of calcium ....	0.09	....	....	0.02	....
„ of magnesium ....	0.28	....	....	....	....
Sulphate of lime ....	....	0.02	0.55	0.11	0.50
„ of soda ....	....	....	0.03	....	....
Carbonate of lime ....	....	....	0.52	0.16	....
„ of magnesia ....	....	....	0.13	0.15	....
Alumina and peroxide of iron ....	....	0.01	0.53	0.80	0.20
	100.00	100.00	100.12	100.05	100.00

	XI.	XII.	XIII.	XIV.	XV.
Chloride of sodium ....	97.0	98.89	98.53	72.16	99.55
„ of calcium ....	....	....	0.93	1.65	trace
„ of magnesium ....	....	1.11	0.54	5.57	....
Sulphate of lime ....	3.0	....	....	10.72	....
„ of magnesia ....	....	....	....	2.06	....
Carbonate of lime ....	....	....	....	3.71	....
„ of magnesia ....	....	....	....	2.89	0.45
Alumina and peroxide of iron ....	....	....	....	1.24	....
	100.00	100.00	100.00	100.00	100.00

	XVI.	XVII.	XVIII.	XIX.	XX.
Chloride of sodium ....	94.57	25.09	94.15	86.13	90.30
„ of magnesium ....	0.97	....	1.56	5.02	....
Sulphate of lime ....	0.89	1.23	1.93	7.04	0.50
„ of magnesia ....	....	42.07	....	....	9.02
„ of soda ....	....	1.57	0.82	....	....
Alumina and peroxide of iron ....	1.12	0.46	....	....	0.20
Residue ....	2.23	1.37	....	....	....
Water ....	0.22	28.21	1.54	3.03	....
	100.00	100.00	100.00	101.22	100.02

I, from Wieliczka, white variety, gave, on being dried, little water.\*

from Hall, in the Tyrol, traces of chloride of potassium. In the last also, and likewise in the salt of several salt-works, he found sal-ammoniac. Gilbert's Annal., Vol. 64, p. 160; and Journ. für pract. Chemie. Vol. 2, p. 294.

\* The water which penetrates into the rock-salt mines at Wieliczka, dissolving more or less of the rock-salt, is, as is known, pumped out and allowed to run into the Vistula. From an analysis communicated by I. N. Irdina (Geschichte



II, from Berchtesgaden, fibrous variety.

III, „ „ yellow variety.

IV, from Hall, in the Tyrol.

V. Crackling salt, from Hallstadt in Austria. It decrepitates when triturated, and effervesces when dissolved in water, numerous small bubbles of gas being at the same time disengaged. In the latter property, it perfectly agrees with the well-known knister (crackling) salt from Wieliczka. It yielded, on being dried, a large amount of water.

VI, from Schwäbisch—Hall.\*

VII, VIII and IX, from Wilhelmsglück at Schwäbisch-Hall, according to Fehling; † VII, pure rock-salt; VIII, IX, impure.

X, from Vic, according to Berthier. ‡

XI, from Djebel Melah, in Algeria, after deduction of 6·6% silica and 0·4% water.

XII, XIII, XIV, from Ouled Kebbab, in Algeria, after deduction of silica and water; XII and XIII, fibrous; XIV, impure, according to Fournet. §

XV, from Holston, in Virginia, according to C. B. Hayden. ||

XVI and XVII, small pieces of rock-salt, which were found in the bore-dust of the bore in Stassfurth, according to Heine; ¶ XVIII and XIX, ditto, according to Grund.\*\*

XX, ditto (so-called martinsite), according to three analyses, agreeing exactly with one another. On being treated with water, a residue was left undissolved, which consisted of gypsum and boracite, chiefly the latter. Martinsite gives out, on being rubbed, a bituminous odour, †† and dissolves in water with very slight effervescence. ‡‡

der Wieliczker Saline, 1842), the saline ingredients it contains, consist of 97·95 chloride of sodium, 0·54 chloride of magnesium, 0·20 sulphate of lime, 0·62 sulphate of magnesia, 0·08 peroxide of iron, and 0·62 of resinous extractive matters. Although we cannot expect this solution to be so pure as the rock-salt submitted to analysis, it being a portion of a specimen which, on account of its purity, had been selected for a mineral collection—a remark which likewise applies to the other specimens of rock-salt analysed by me—yet it shows the great purity of the rock-salt at Wieliczka in general.

\* I to VI, according to my analyses. These specimens, which I owe to the kindness of Dr. Krantz, were dried at a temperature of 212°. They dissolved without residue in water.

† Württembergische naturwissenschaftliche Jahreshefte. Vol. 4, p. 36.

‡ Annales des Mines. 1825. Vol. 10, p. 259.

§ Ibid. 1846. 4 series. Vol. 9, p. 546.

|| The American Journal of Science. 1843. Vol. 44, p. 179.

¶ Archiv. für Mineralogie, Vol. 19, pp. 365 and 366.

\*\* Ibid.

†† Monats-Berichte der Berliner Acad. 1847. Januar.

‡‡ By the middle of December, 1846, 154½ feet of rock-salt had been already

Joss\* found bromine in the Hungarian rock-salt. According to O. Henry,† almost all rock-salt contains iodine. Sulphate of magnesia, sulphate of soda, blödite, löwite, glauberite, polyhalite, fluorspar, apatite, and boracite, sometimes, but very rarely, accompany rock-salt and gypsum.

The specimens of rock-salt I to XIII and XV are distinguished for their remarkable purity.‡ XIV and XVI to XX are on the other hand, more or less impure.

Schrötter and Pohl§ analysed two sorts of commercial sea-salt: I, from the salt manufactory, or marinhas (Salzgarten), of St. Felice, at Venice; II, from that of Trapani in Sicily. Both on being treated with water left residues which consisted of lime, alumina, peroxide of iron, magnesia, phosphoric and carbonic acids, and quartz-sand. The filtered solution contained no carbonates nor phosphates; it was also free from bromine, iodine, and fluorine. Göbel|| analysed the salt which is deposited upon the bottom of the Elton Lake, III.

		I.	II.	III.
Chloride of sodium ....	....	98·95	98·94	98·79
„ of magnesium ....	....	0·19	0·16	0·13
„ of potassium ...	...	...	...	0·04
Sulphate of lime ....	....	0·51	0·46	1·04
„ of magnesia ....	....	0·35	0·44	...
		100·00	100·00	100·00

In the proportion of chloride of sodium, as also in their general composition, these three deposits agree so closely with the preceding specimens of rock-salt, that no one will doubt the possi-

passed through: the proportion of sulphate of magnesia, and especially of the earthy admixtures, had, however, been always increasing. A very considerable increase in the quantity of chloride of magnesium had also taken place. The latter salt is formed, according to Karsten, from chloride of calcium, as is shown by the numerous newly formed lamellæ of gypsum which are constantly issuing from the bore along with the brine. (Karsten, in Poggendorff's *Annal.* Vol. 70, p. 557.)

\* *Journ. für pract. Chem.* Vol. 1, p. 129.

† *Journ. Chim. Med.* Vol. 5, p. 81.

‡ This is also the case with the rock-salt at Illetskaia-Zastchita, in the Steppes of the Kirghis. It is crystalline, white, without a stain, and so pure that the salt is at once pounded for use, without any cleansing or re-crystallization. Murchison, *Geology of Russia.* Vol. 1, p. 184.

§ *Berichte der Wiener Acad.*, Vol. 6, p. 224. The sulphate of soda given in this analysis, has been reduced to sulphate of magnesia, and the water deducted.

|| G. Rose, *Reise nach dem Ural.* Vol. 2, p. 264.

bility of these also having been at one time formed by deposition from the sea-water.

T. Usiglio\* submitted a portion of the water of the Mediterranean to evaporation under circumstances similar to those under which it takes place during the process of obtaining the salt, and examined the deposits at different degrees of concentration. In the following table an abstract of the results of his researches has been given.

SALTS DEPOSITED, IN GRAMMES.

Volume of evaporated water.	Peroxide of Iron.	Carbonate of Lime.	Sulphate of Lime with Water of Crystallization	Chloride of Sodium.	Sulphate of Magnesia.	Chloride of Magnesium.	Bromide of Sodium.
46.7%	0.003	0.064					
81.0		0.053	0.560				
90.5			0.957	3.261	0.004	0.008	
96.1			0.218	17.546	0.039	0.079	0.073
97.			0.014	2.624	0.017	0.015	0.036
98.4				3.676	0.563	0.051	0.114
Sum ...	0.003	0.117	1.749	27.107	0.623	0.153	0.223

Supposing that in obtaining the salt I, so much chloride of sodium is deposited as is separated on evaporation to the extent of 96.1%, in the mother-liquor which remains, according to the analysis of the sea-water from the Lagunes of Venice, the proportion of chloride of magnesium is 6.6%, that of sulphate of magnesia 7.1%. From such a mother-liquor, containing so much of both salts, a chloride of sodium separates which contains only 0.19% of chloride of magnesium, and only 0.35% of sulphate of magnesia. From the Elton Lake water, which in August contains 22% of chloride of magnesium, and 3% of sulphate of magnesia, a chloride of sodium is deposited which contains only 0.13% of chloride of magnesium, and no sulphate of magnesia at all. Although, therefore, at the time when the rock-salt was deposited, the sea-water had been so much concentrated that the chloride of magnesium and sulphate of magnesia were present in the above-mentioned proportions, a chloride of sodium might, notwithstanding, have been deposited which contained either none, or only minute traces of these salts. The great purity of rock-salt, then, instead of being an objection to the supposition that it is formed by deposition from the sea-water, is rather an argument in favour of it.

\* Annal. de Chimie et de Phys. (3). Vol. 27, p. 172.

The chloride of potassium in the sea-water of the Lagunes of Venice amounts to 2·86% of the entire solid ingredients; in neither of the two analyses of the salt obtained from the water of the Mediterranean, however, is it indicated. If we again suppose that in the preparation of the salt at the manufactory of St. Felice 96·1% of water is carried away by evaporation, in the 3·9% of mother-liquor which remains the chloride of potassium amounts to 2·1%. From such a mother-liquor, therefore, a chloride of sodium is deposited which contains no chloride of potassium. The chloride of potassium in the water of the Elton Lake is 0·9% of the entire solid constituents; Göbel found, however, in the salt deposited by the water only 0·04%; consequently, here also only a very inconsiderable amount of chloride of potassium had been deposited along with the chloride of sodium. What has just been stated with regard to chloride of magnesium and sulphate of magnesia, also applies to the fact, that chloride of potassium is either entirely wanting, or present only in minute quantities in rock-salt.

Even from brine evaporated at the boiling point a salt is obtained which approaches rock-salt in composition. According to the analyses undertaken by Heine\* of the salt produced at the Prussian salt-works in the province of Saxony, the proportion of chloride of sodium in the best sorts varied between 97·14 and 98·67%.

Usiglio's researches show, as might have been expected, that in evaporating sea-water most of the sulphate of lime separates before the deposition of chloride of sodium commences, and that this only begins when the evaporation has proceeded so far that the concentrated sea-water forms a saturated solution of salt. The magnesian salts which he found in the common salt which was deposited, were undoubtedly held in solution by the mother-liquor with which the salt was impregnated, inasmuch as the sulphate of magnesia crystallises only in the cold, while the chloride of magnesium cannot be brought to the crystalline state at all.†

When a solution of chloride of magnesium is evaporated at the ordinary temperature, this salt can never be deposited in the solid form. We shall afterwards see that the evaporation of such a solution ceases to go on so soon as it has reached a certain maximum. Had the sea-water, therefore, been at any time concentrated

\* Karsten's and von Dechen's Archiv. für Mineralogie, &c. Vol. 19, p. 1, et seq.

† That the bromide of magnesium should exceed the chloride, is opposed to all previously known facts.



by evaporation to this maximum, the salt deposited would have remained always covered by a concentrated solution of chloride of magnesium, unless some means had been afforded by which this might have drained away. Such might have taken place by an elevation of the bottom of the seas on which the salt had been deposited. Since, however, rock-salt in by far the greatest number of instances is covered by sedimentary rocks, often of great thickness, the organic remains in which indicate their having been formed by deposition from the sea, it is clear that these rocks must have partly displaced and partly absorbed the solution in question.

Chloride of magnesium being, next to chloride of sodium, the most predominant of the saline constituents of sea-water, and being, therefore, present in a very great quantity, the circumstance that it can occur upon the earth's surface only in the state of solution, deserves attention. It is only at such depths beneath the earth's surface where a temperature exceeding that of boiling water prevails, that it can be supposed to exist in the solid form. If the sedimentary formations extend to these depths, the solution of chloride of magnesium with which they were impregnated during their formation will then have been dried up. That the transition rocks reach far greater depths there cannot be the slightest doubt; it is probable, however, that even the more recent sedimentary formations also extend so far.

In the mother-liquor of sea-water sulphate of magnesia may assume the crystalline form, and that this has under certain circumstances actually taken place, No. XVII and XX of the rock-salt analyses show. Since in XVII the rock-salt consisted of fragments found in the rubbish obtained during the operation of boring; and as the amount of sulphate of magnesia much exceeds that of the chloride of sodium, while in XX the former falls much below the latter, it would appear that the sulphate of magnesia diminishes as the depth increases, XVII having been taken from a comparatively small, XX, on the contrary, from a comparatively great depth. This seems to be opposed to the statement already made, that in the bore, which had passed through  $154\frac{1}{2}$  feet of rock-salt, the proportion of sulphate of magnesia had been found to be always increasing. The bore in question, however, has since 1847 been continued to a depth of 1000 feet, and pure salt actually been reached. In this case also, therefore, we have a confirmation of the theory that, keeping gyp-

sum out of view, chloride of sodium is the first deposit which takes place from the sea.\*

The almost entire absence of chloride of potassium from rock-salt† is explained by the circumstance of its being more easily soluble in water than chloride of sodium. As regards the other substances which are held in solution in sea-water in exceedingly minute quantity, these for the most part undoubtedly remained in the mother-liquor along with chloride of magnesium and sulphate of magnesia. It is therefore probable, that if attention be directed to this point, such substances will be found in those rocks which have been formed by deposition from the sea. In the oolitic limestone at Lyons, iodine has been actually detected by Lemberg.‡

Since the deposition of rock-salt from sea-water, changes have still been effected through the agency of water, as is shown by the pseudomorphs of anhydrite, gypsum, and polyhalite in the form of rock-salt. According to Haidinger,§ there are found at Hall, in Tyrol, spaces closely compressed, which formerly contained rock-salt, but are now filled with granular anhydrite. In the saliferous clay of this place, as well as in that at Hallein, Aussee, Hallstadt, &c., cubes of rock-salt occur which, for the most part, have been more or less altered by pressure. In the marl-slate of Gössling, at Weyer, in Upper Austria, Haidinger found such cubes filled with gypsum, and surrounded by an incrustation of dolomite. Similar structures also occur in the marl of the rock-salt formation of Soovar, in Hungary. Water, holding in solution sulphate of lime, must have dissolved the rock-salt, and deposited the sulphate of lime as gypsum or anhydrite in its place. When, also, the water contained carbonate of lime and carbonate of magnesia, these carbonates were deposited together as dolomite. Some of the cubes from Soovar are found surrounded by an incrustation of dolomite which retains their form, and have in their interior a single gypsum crystal which has displaced the rock-salt. All these furnish examples which are quite in accordance with the law, that bodies which are difficultly soluble displace those which are easily soluble (p. 40).

Polyhalite, a salt consisting of sulphate of lime, sulphate of

\* Should I succeed in obtaining specimens of this rock-salt, from its analysis it would be seen whether it be as free from sulphates of magnesia as the previously analysed specimens of rock-salt.

† Although I have employed the greatest care in examining for this salt, only in the knister-salz of Hallstadt have I found traces of it.

‡ Journ. de Pharm. et de Chimie (3). Vol. 19, p. 240.

§ Poggendorff's Annal., Vol. 52, p. 625.

magnesia, and sulphate of potash, occurs in rock-salt formations (Ischel, Berchtesgaden, and Aussee). Berthier\* found a similar salt in the rock-salt bed of Vic, in Lorrain, which contained soda instead of potash. These salts have not probably been deposited together with the rock-salt, but are more recent formations; for, according to Haidinger,† there occur in the saliferous clay of Aussee cubes whose nucleus alone consists of rock-salt, while their thick crust consists of polyhalite. In regard to this polyhalite, at least, there can be no doubt that it has at a subsequent period been deposited by water, which had dissolved the sulphates it contains out of rock-salt formations.

If such displacement of chloride of sodium by sulphates be a general process, the composition of the brines by which it is effected must thereby be essentially changed. They must become richer in chloride of sodium, and poorer in sulphates. In this way the origin of brines which are often so poor in these salts would be explained.‡

The so-called crystallized sandstones which occur between Esslingen, Stuttgart, and Tübingen, in many parts of the red or variegated marls, have been long known;§ they occur in a

\* Ann. des Mines. Vol. 10. p. 260.

† Holger's Zeitschrift für Physik., &c. Vol. 4, p. 226.

‡ Haidinger (Poggendorff's Annal., Vol. 71, p. 247) completes his earlier communications by several new observations. At Hallein there was found a large deformed rock-salt cube, the interior of which was filled with crystals of anhydrite. At Pirano there occurred a marl, containing cube-shaped cavities, which were lined with small crystals of anhydrite, in the same manner as is seen in druses. Disfigured cubes, 2 to 3½ inches in size, from Aix, in Provence, were found to be entirely composed of lenticular crystals of gypsum, 2 to 3 lines in size. Nöggerath (Jahrbuch für Mineralogie, &c., 1846, p. 309) had already described these disfigured cubes as gypsum-pseudomorphs in the form of rock-salt. It is only in rare instances that their faces are at right angles to each other: for the most part, they have more or less of a rhomboidal form, although they cannot be regarded as regular rhomboids, inasmuch as not only are the angles at their edges sometimes more acute, sometimes more obtuse, but different edges of one and the same crystal exhibit numerous irregularities. There can be no doubt that all these crystals were originally cubes which have undergone various degrees of pressure, and have in consequence taken a modified form. According to the information kindly conveyed to me by Nöggerath, many cubes of iron pyrites occurring in the clay-slate at Montjoie, in the neighbourhood of Aix-la-Chapelle, show similar disfigurations. They are from 2 to 15 lines in size, and very rarely are they rectangular. Frequently the pressure of the mass of clay-slate has given rise to very different angles, so that these crystals, like those in the form of rock-salt, resemble rhomboids more than cubes. No doubt many more such pseudomorphs as those above mentioned in the form of rock-salt will be found, when attention is more directed to this subject. The probability that the processes are general by which rock-salt is displaced, will then become more surely confirmed.

§ Alberti, Monographie des bunten Sandsteins. Muschelkalks an 1 Keupers. 1834, pp. 147 and 186.

sandstone layer, and are sometimes so small as to be visible only with the microscope, but occasionally from 1 to  $1\frac{1}{2}$  inch in size. The lateral surfaces of the cubical crystals are always more or less pressed in and concave. According to Gaup, the Würtemberg pseudomorphs consist of 72·6 silica, 23·6 alumina, 0·7 lime, 0·6 peroxide of iron, 2·5 loss by combustion: they are, therefore, true silicates of alumina. Such sandstone crystals also occur in various other places, as below Eicks in the Eifel, where they are found between the red or variegated sandstone, and the muschelkalk, at Igel, near Trèves, &c. In the latter place the sandstone beds, which contain the crystallized sandstone, alternate with beds of gypsum, in which only traces of rock-salt have been found.

Nöggerath, from his opinion that the irregular rock-salt crystals from the salt-formations at Berchtesgaden are disfigured cubes which have, whilst in a partially soft state, or during their formation, undergone compression in the saliferous clay with which they are surrounded, holds that these sandstone-cubes, which are also chiefly disfigured, were originally rock-salt cubes, the chloride of sodium in which has been displaced by the sandstone. Blum\* and Haidinger† agree with this view; it has also been confirmed by the researches of Paulus,‡ made at the same time as those of Nöggerath.

Hausmann§ describes limestone, occurring in the muschelkalk regions upon the Weser, in the form of rock-salt, from 1·4 to 3·5 inches in size, which, however, according to Wöhler, do not contain a trace of common salt. They are found exactly in that part of the muschelkalk which, in Germany, incloses the rock-salt. According to the observations of Strüver, these pseudomorphs do not occur merely as single isolated crystals, but form (upon the Feldberg, near Hohe, and in the surrounding country of Bodenwerder) whole beds, and not merely in a single limestone layer, but in several adjacent layers, always too in the neighbourhood of gypsum layers. According to C. List, they contain 61·19 parts of carbonate of lime, 22·501 of carbonate of magnesia, 16·301 insoluble silicate of alumina, and 0·008 chloride of sodium. The so-called crystallized sandstones from the neighbourhood of Cassel

\* Nachtrag. zu den Pseudomorphosen, p. 127.

† Loc. cit., p. 259.

‡ Würtembergische naturwissenschaftliche Jahreshefte. 1846. Vol. 2, p. 196. Paulus found, particularly in the Kornthal, in Würtemberg, similar, but much more perfect crystals upon a hard marl above the gypsum of the red or variegated marls, and always, indeed, upon the under surface of the layers which were sunk in clay. They consisted entirely of marl.

§ Nachrichten von der Universität. und der Gesellschaft der Wissenschaften in Göttingen. 1846. Nos. 8 and 17.



are, for the most part, according to Haidinger, crystallized compact limestones. Hausmann mentions, on the authority of Professor Eaton,\* the occurrence of similar pseudomorphous spaces in the marls of the salt-formations in the super-silurian rocks near Syracuse, in North America. They are not true pseudomorphs, but impressions left in the soft chalk-marl by common salt-pyramids, as also in the red or green marl-slate, in which they occur in great perfection, and in immense quantities. Thousands of such empty spaces, some 5 inches in diameter, are seen in Manlius Center especially, upon the southern declivity of the Erie Channel, and in other places.

The marl-pyramids in the marl of Montmartre at Paris, are also regarded by Haidinger as pseudomorphs in the form of rock-salt. The impressions of turritella, corbula, &c., found in this marl, in like manner indicate a salt-water origin.

Gutberlett† shows that the pseudomorphs, in the form of rock-salt, cover the plains of strata of great extent, and are repeated in more than fifty strata, overlying one another, as is especially the case in the neighbourhood of Fulda. The strata in question consist of variegated marl, interposed between the new red sandstone and muschelkalk. For the most part, the rock-salt appears to be replaced by siliceous masses, particularly by sandstones of very different kinds, and by quartzite. Mica and brown-spar also appear as replacing substances. In the immediate neighbourhood of these pseudomorphs no rock-salt has as yet been found: the pseudomorphs themselves, however, are evidences of its having formerly been present. Flatly compressed casts of *Terebratulæ* are found in large numbers, partly in the pseudomorphous, and partly in the other layers. In the above-mentioned layers upon the Feldberg, &c., however, no petrefactions occur together with the pseudomorphs.

Haidinger supposes the formation of the sandstones, in the form of rock-salt, to have taken place in the following manner: upon the surface of a mud-sediment left by the sea, after the evaporation of the sea-water, rock-salt crystallized in cubes, which left the impression of their surfaces and angles in the soft mud; subsequently, this sediment became covered with sand, which enclosed the rock-salt cubes, and after these were gradually redissolved, the sand passed into the spaces they occupied, and was

\* Silliman's American Journ. Vol. 15, No. 2, Jan., 1829.

† Jahrbuch für Mineralogie, &c. 1847, pp. 405 and 513.

cemented by the silicic acid held in solution in the water. There are few facts which controvert this opinion.

When we consider that the pseudomorphs,\* and impressions in the form of rock-salt, occur in all saliferous formations, in the super-silurian strata, in the marl-slate of the zechstein,† in muschelkalk, in red or variegated marls,‡ in Alpine limestone, and in the miocene strata of Parisian gypsum, their great geological importance will at once become apparent.

They afford just as decided a proof of the formation of these rocks from sea or salt-water, as is afforded by the remains of marine animals; they show, also, that during the great sedimentary period, from the deposit of the transition-formations to those of the tertiary, rock-salt has, with perhaps a few interruptions, been deposited. That which is surrounded by impermeable strata, has been preserved up to the present time; that, however, which was deposited in greater or smaller crystals in rocks, was gradually dissolved by percolating water, and again conveyed into the sea, while the empty spaces thus left were either filled with different mineral substances, or remained empty. That even at the present time remains of rock-salt still occur in these rocks, is shown by the circumstance of its existing in such quantity, at least, as to admit of being detected by reagents, in the springs which proceed from them.

Very different from the composition of rock-salt is that of most brines, analyses of which we possess in great number. Several of the older analyses, made at a time when the analytic process was but imperfectly understood, have been omitted. With a view to facilitate the comparison of the composition of the brines with that of rock-salt, I have reduced the constituents,

\* The sandstones in the form of rock-salt are distinguished from the true replacement-pseudomorphs by the circumstance that the substances in the latter have been brought by the water in a dissolved, those in the others in an undissolved state. For the sake of distinction, the latter might be termed mechanical pseudomorphs. A defined boundary line between these two species of replacement-pseudomorphs cannot, however, be drawn. The cementation of the sand, which has passed into the empty spaces, into sandstone, shows that silica has also passed in a state of solution. The filling of these spaces with quartzite and brown-spar can only be explained in this manner; and in cases where they are filled with limestone and marl, these must also, in part at least, be explained in the same manner. That the mica in these pseudomorphs has been introduced in a mechanical way, is less probable than the view that it has been generated by the metamorphosis of substances previously introduced.

† Ph. Braun, im neuen Jahrbuch für Mineralogie, &c. 1846, p. 814.

‡ M. S. Fournet (Histoire de la Dolomie, 1847, p. 117) found them also in the group of the red sandstone in the region of Lyon, upon Mont d'Or, at Chessy, and at Blacet, not far from Villefranche.

which, in general, are given in the proportions in which they are contained in 100 parts of the brine, to the per-centage in which they exist in the solid constituents.\* Since, however, the greater or smaller amount of the saline ingredients contained in brines, constitutes an essential character by which their mode of formation is ascertained, the general amount contained in each of the brines has been given.

*Brines in Prussian Saxony.*

	I.	II.	III.
Amount of salts ... ..	12.28	18.89	8.20
Chloride of sodium ... ..	94.43	93.79	91.81
" of magnesium ... ..	1.69	2.15	2.71
" of calcium ... ..	1.03	0.71	1.17
" of potassium ... ..	0.21	0.88	0.20
Sulphate of lime ... ..	2.23	2.47	3.28
Carbonate of lime ... ..	0.37	...	0.52
" of iron ... ..	0.02	...	0.25
Fossil resin ... ..	0.02	...	0.06
	100.00	100.00	100.00

	IV.	V.	VI.
Amount of salts ... ..	8.42	3.77	17.16
Chloride of sodium ... ..	87.33	94.03	94.49
" of magnesium ... ..	5.55	1.97	0.99
" of calcium ... ..	2.04	1.05	...
" of potassium ... ..	1.92	...	...
Bromide of magnesium ... ..	...	0.02	...
Sulphate of lime ... ..	3.16	2.66	2.80
" of magnesia ... ..	...	...	1.20
" of potash ... ..	...	...	0.34
Carbonate of lime ... ..	...	0.27	0.18
" of iron ... ..	...	...	trace
Silica ... ..	...	...	trace
	100.00	100.00	100.00

\* These numbers do not, of course, represent the composition of the impure rock-salt as contained partly in gypsum, partly in saliferous clay, and partly in

	VII.	VIII.	IX.
Amount of salts ....	2.00	11.10	4.86
Chloride of sodium ....	95.71	93.72	91.44
" of magnesium ....	1.09	0.67	0.60
" of potassium ....	0.08		
Sulphate of lime ....	1.61	2.55	3.31
" of magnesia ....	0.20	1.18	1.26
" of potash ....	0.08	1.34	2.24
" of soda ....	1.17		
Carbonate of lime ....	0.04	0.44	0.82
" of magnesia ....		0.05	0.25
" of iron ....	0.02	0.03	0.04
Silica ....		0.02	0.04
	100.00	100.00	100.00

	X.	XI.	XII.	XIII.
Amount of salts ....	3.006	26.50	8.39	3.34
Chloride of sodium ....	81.44	95.35	89.88	81.97
" of magnesium ....	2.03	1.59	1.49	
" of potassium ....		0.45		
Sulphate of lime ....	14.29	1.51	0.04	9.99
" of magnesia ....	0.30		0.63	2.27
" of potash ....	1.76	1.10	0.99	0.90
" of soda ....				4.21
" alumina ....			6.77	
Carbonate of lime ....	0.18		0.15	0.63
" of magnesia ....			0.02	trace
Peroxide of iron ....			0.01	0.03
Silica ....			0.02	
	100.00	100.00	100.00	100.00

rocks, inasmuch as the difficultly soluble salts, especially the sulphate of lime, will be taken up by the percolating water in much smaller quantity than those which are easily soluble. If then sulphate of lime be generally found in brines, it must be regarded as existing in the rocks in much greater proportion. Many brines certainly arise in saliferous gypsum.



	XIV.	XV.	XVI.	XVII.
Amount of salts ....	4.96	3.38	1.82	1.73
Chloride of sodium ....	87.60	81.99	74.79	74.65
Sulphate of lime ....	8.83	10.66	10.99	12.03
„ of magnesia ....	2.08	2.73	4.76	4.31
„ of potash ....	0.62	0.72	0.99	0.91
„ of soda ....	0.57	2.28	6.93	6.18
Carbonate of lime ....	0.28	0.78	1.26	1.66
„ of magnesia ....	trace	0.54	0.06	0.03
Peroxide of iron ....	0.02			
Silica ....		0.30	0.22	0.23
	100.00	100.00	100.00	100.00

*Brines in Prussian Westphalia.*

	XVIII.	XIX.	XIX.a
Amount of salts ....	4.25	7.28	6.92
Chloride of sodium ....	80.80	89.52	91.47
„ of magnesium ....	0.65	1.84	1.71
„ of calcium ....	...	3.47	2.14
„ of potassium ....	...	0.03	
Bromide of magnesium ....	0.008	trace	
Sulphate of lime ....	7.04	2.79	3.22
„ of magnesia ....	6.93	...	
„ of potash ....	0.11	...	
Carbonate of lime ....	2.52	1.39	1.46
„ of magnesia ....	1.67	0.21	
„ of iron ....	0.16	0.26	
„ of manganese ....	0.002	...	
Silica ....	0.11	0.49	
	100.000	100.00	100.00

I to V. Brines from Halle on the Saale. I, Deutscher Brunnen, according to Meissner; II, Gutjahr Brunnen, according to Heine;\* III and IV, Hacke Brunnen, according to Herrmann and Heine, from a depth of 62 feet; V, Wettekind near Halle, according to O. L. Erdmann.†

VI. Brine from Stassfurth, from a pit 105 feet deep, according to Heine.

VII to IX. Brines of Schönebeck. VII, for medicinal use,

\* Archiv. für Mineralogie, &c. Vol. 19, p. 1, et seq.

† Journ. für. pract. Chemie. Vol. 46, p. 313.

according to Herrmann; VIII, brine from the pit No. III; IX, from the pit IV, according to Heine.

X and XI. Brines from Artern; X, from the brine-spring in the Salzthal; XI, from the bore in the rock-salt.

XII. Brine from Dürrenberg, from the pit at the depth of 56 feet.

XIII and XIV. Brines of Kösen. XIII, from the old pit at a depth of 484 feet; XIV, from the new pit, at a depth of 515 feet.

XV. Brine from the main pit at Kötzschau, at a depth of 46 feet.

XVI and XVII. Brines of Teuditz. XVI, from the main pit, from a depth of 55 feet; XVII, from Dünkler's pit-shaft, from a depth of 10 feet.

The analyses X to XVII, which were conducted with great care, are all by Heine.\*

XVIII. Brine from the bore at Neusalzwerk, near Prussian Minden, according to an analysis by me. From this brine much carbonic acid is evolved.

XIX. Brine of Werl, according to Ferd. Deneke.†

XIX a. Brine of Königsborn, at Unna.‡

*Brines in Saxe-Weimar.*

	XX.	XXI.	XXII.
Amount of salts ....	3.70	3.42	4.39
Chloride of sodium ....	83.47	81.62	91.24
„ of potassium ....	0.32	0.32	0.72
Sulphate of lime ....	7.41	9.66	3.38
„ of magnesia ....	4.00	3.05	0.78
„ of soda ....	2.56	4.41	2.53
Carbonate of lime ...	0.57	0.33	0.40
„ of iron ....	1.67	0.91	0.95
	100.00	100.30	100.00

XX. Mühlenquelle; XXI, Kunstgrabenquelle; XXII, Leopoldsquelle in Stadt-Sulza, according to F. Miller.§

\* Loc. cit.

† Annal. der Chem. und Pharmacie. Vol. 65, p. 100.

‡ Karsten, Salinenkunde. Vol. I, p. 240.

§ Archiv. der Pharmacie (2) Vol. 57, p. 165. The chlorides of magnesium and calcium, as also the sulphate of soda, given in the original analysis, have been here reduced to chloride of sodium, sulphate of magnesia, and sulphate of lime.

*Brines in Hesse and Hanover.*

	XXIII.	XXIV.	XXV.	XXVI.
Amount of salts ....	2·37	2·98	3·14	10·53
Chloride of sodium ....	82·23	77·38	86·95	90·84
„ of magnesium ....	1·18	12·62	8·45	1·42
„ of potassium ....	1·83	3·37	...	...
„ of calcium ....	6·74	...	...	...
Bromide of magnesium ....	0·04	0·30	0·31	...
Sulphate of lime ....	0·18	2·11	0·15	3·26
„ of magnesia ....	...	...	...	1·97
„ of soda ....	...	...	...	1·75
Carbonate of lime ....	7·43	3·68	4·07	0·52
„ of iron ....	0·23	0·41	0·05	...
„ of manganese ....	0·07	...	...	...
Silica ....	0·07	...	...	0·07
Silicate of soda ....	...	0·13	0·02	...
Asphalt-like substance ....	...	...	...	0·17
	100·00	100·00	100·00	100·00

XXIII. Great Soolsprudel, at Nauheim, contains traces of organic substances. The carbonates are calculated as bicarbonates, according to C. Bromeis.\*

XXIV. Brine No. II; at this place, according to Figuier and Mialhe.†

XXV. Brine No. V; at this place, according to the same.

	XXVII.	XXVIII.	XXIX.	XXX.
Amount of salts ....	1·33	1·85	1·57	1·27
Chloride of sodium ....	80·07	86·49	91·29	86·01
„ of magnesium ....	8·92	7·03	1·98	2·24
„ of potassium ....	0·23	0·15	1·32	1·81
Sulphate of lime ....	0·20	0·10	0·60	0·65
Carbonate of lime ....	7·07	5·54	3·44	7·73
„ of magnesia ....	2·71	...	0·69	0·77
„ of iron ....	0·32	0·52	0·29	0·29
Silicate of soda ....	0·48	0·17	0·39	0·50
	100·00	100·00	100·00	100·00

\* Jahresbericht der Wetterauischen Gesellschaft. 1846, p. 47.

† Journal der Pharmacie (3). Vol. 13, p. 401.

XXVI. Brine containing sulphuretted hydrogen, at Lindener Berg, near Hanover, according to Bromeis.\*

XXVII. Elisabethquelle, at Homburg.

XXVIII. Kaiserquelle, in the same place.

XXIX and XXX. Brines at Soden; XXVII to XXX according to Figuier and Mialhe.†

*Brines in Würtemberg.*

	XXXI.	XXXII.	XXXIII.	XXXIV.
Amount of salts ....	26.04	26.39	25.92	24.00
Chloride of sodium ....	98.17	98.17	99.22	97.81
„ of magnesium ....	0.02	trace	...	trace
Sulphate of lime ....	1.68	1.68	0.66	2.12
„ of magnesia ....	0.09			
„ of soda ....	...	0.08	0.11	
Carbonate of lime ....	0.04	0.07	0.01	0.07
	100.00	100.00	100.00	100.00

	XXXV.	XXXVI.	XXXVII.
Amount of salts ....	26.12	25.66	25.79
Chloride of sodium ....	98.11	98.02	98.02
„ of magnesium ....	trace		
„ of calcium ....	1.76	0.05	0.10
Sulphate of lime ....	0.02	1.82	1.77
Carbonate of lime ....	0.11	0.11	0.11
	100.00	100.00	100.00

\* Annal. der Chemie und Pharmacie, Vol. 69, p. 115. The chloride of magnesium and sulphate of soda given in this analysis have been partly reduced to chloride of sodium and sulphate of magnesia.

† Loc. cit.



XXXI. Of Friedrichshall.

XXXII. Of Clemenshall.

XXXIII. Of Hall.

XXXIV. Of Sulz.

XXXV. Of Wilhelmshall, at Rottenmünster.

XXXVI and XXXVII. Brines from two bores of Wilhelmshall, at Schwenningen.\*

*Brines in Bavaria.*

	XXXVIII.	XXXIX.	XL.
Amount of salts ....	23·30	1·11	·04
Chloride of sodium ....	96·99	76·05	75·30
„ of magnesium ....	0·20	6·07	6·85
„ of potassium ....	...	1·18	0·62
„ of ammonium ....	0·01		
Bromide of magnesium ....	0·01	0·59	0·63
Sulphate of lime ....	1·79	3·24	3·13
„ magnesia ....	0·73	2·00	1·60
„ of potash ....	0·26		
Carbonate of lime ....	0·004	6·47	9·37
„ of magnesia ....	trace	2·94	1·88
„ of iron ....	0·003	0·88	0·62
Silica ....	0·005	0·58	
	100·002	100·00	100·00

XXXVIII. Edelsoole of Reichenhall, according to Buchner, junior.†

XXXIX and XL. Brines at Kissingen; II, Ragozibrunnen; III, Pandur; both according to A. Vogel.‡ From these brines much carbonic acid is evolved. From the unusually large amount of carbonate of lime, it may be presumed that a portion of the lime was combined with sulphuric acid.

\* These seven analyses are by Fehling (*Chemische Untersuchung der Soolen des Stein- und Kochsalzes etc. der Württembergischen Salinen*, 1847).

† *Repertorium der Pharmacie* (3), Vol. 6, p. 30. This brine seems to be the one which is conducted from Berchtesgaden to Reichenhall, and which is there obtained from the saliferous clay. Its great purity, as well as the large proportion in which the chloride of sodium is present, indicate at least that it proceeds from rock-salt.

‡ *Mineralquellen des Königreich's Baiern*, 1829.

*Brines in England.*

	XLI.	XLII.	XLIII.
Amount of salts ....	0.92	0.82	1.06
Chloride of sodium ....	74.53	53.08	80.90
Bromide of sodium ....	0.51		
" of magnesium ....	...		0.41
" of calcium ....	...	0.35	
Iodide of magnesium ....	...		0.06
Sulphate of lime ....	...	1.99	
" of magnesia ....	...	11.63	1.37
" of potash ....	0.46		
" of soda ....	17.48	25.19	11.19
Phosphate of iron ....	...	0.03	
Carbonate of soda ....	3.13		
" of lime ....	1.19	3.86	2.30
" of magnesia ....	1.76	0.34	0.92
Organic extractive matters, and Quellsäure ....	0.51	2.94	2.48
Silica ....	0.43	0.18	0.37
	100.00	99.59	100.00

XLI. Pitville-water, contains a trace of iodide of sodium, according to Abel and Rowney.\*

XLII. Sulphuretted water No. I, Royal Old Wells, according to the same\*.

XLIII. No. IV, Old Wells, according to the same.\* In these Cheltenham-waters there is free carbonic acid, with traces of phosphate of lime and sulphuretted hydrogen.

These brines are remarkable on account of the presence of a large amount of sulphate of soda, and XLI and XLIII on account of the total absence of sulphate of lime. Had this salt been originally present in XLI it would have been converted by the carbonate of soda into sulphate of soda. These waters, moreover, differ so much in composition from all the others, and possess so small an amount of saline constituents, that they might be regarded rather as mineral-springs containing a large proportion of chloride of sodium, than as proper brines.

The brine-springs of Cheshire are the richest in England, those of Northwich being almost saturated. Those of Barton, also, in

\* Chem. Soc. Quarterly Journ. Vol. 1, p. 193. The chloride of magnesium (XLII and XLIII), and the chloride of calcium (XLII), and the sulphate of soda, have been reduced to chloride of sodium, sulphate of magnesia, and sulphate of lime.

Lancashire, and Droitwich, in Worcestershire, are extremely rich.\* I am not acquainted with any analyses of these brines. Since they are so rich, however, it is to be presumed that they derive their origin from beds of rock-salt, and that they contain little other saline ingredients.

*American Brines.*

	XLIV.	XLV.	XLVI.	XLVII.	XLVIII.
Amount of salts ....	3.67	7.64	4.09	7.05	6.07
Chloride of sodium ....	48.61	84.31	78.24	71.21	77.68
„ of magnesium ....	13.83	...	7.17	4.53	5.16
„ of calcium ....	34.91	...	13.66	23.35	15.91
„ of potassium ....	0.25	0.39			
„ of barium ....	...	...	0.93	0.91	1.25
Bromide of magnesium ....	0.28	...			
„ potassium ....	...	0.22	trace	...	trace
Iodide of sodium ....	...	0.02			
Sulphate of lime ....	2.12				
„ of potash....	...	0.06			
Carbonate of soda ....	...	2.31			
„ of lime ....	...	1.54			
„ magnesia ....	...	6.77			
Alumina ....	...	trace			
Silica ....	...	0.56			
Free carbonic acid ....	...	3.82			
	100.00	100.00	100.00	100.00	100.00

XLIV. Lancaster salt-spring in Canada West, according to J. S. Hunt.†

XLV. Salt-spring of the Caledonia—mineral-springs in Canada.

XLVI, XLVII and XLVIII. Brines from bores which were sunk in coal-formations on the western declivity of the Alleghany mountains, according to analyses kindly communicated by Ch. Lenny in Philadelphia. III, from a bore on the Alleghany river, three miles above Tarentum, 430 feet in depth; IV and V from bores 650 and 680 feet in depth, situated below Tarentum, at a distance of 200 paces from each other; the former yielded much petroleum, the latter none.

Lenny was led to make these investigations from the circumstance that, although the brines extend over a territory of not less than 2,000 English square miles, they do not contain the slightest trace of sulphates. In Germany the only brines in which no sul-

\* Lyell, Princ., p. 249.

† Silliman, American Journ. (2). Vol. 8, p. 364, and Vol. 9, p. 449.

phates are present are those of Kruznach and Münster-am-Stein. The warmest of the brines of Münster proceeds from the red porphyry and from the mouth of the bore of this brine a mixture of carburetted hydrogen, oxygen, and nitrogen gases is exhaled. In the immediate neighbourhood, coal-formations occur from which the carburetted hydrogen is probably derived. It is, therefore, very probable that the brines have also the same origin. Here, consequently, appear to be relations similar to those in the United States.

The remarkable occurrence of chloride of barium in these brines, the first in which it has been found, indicates the impossibility of sulphates being present.

Since, in the rule, the proportion of saline constituents is greater the deeper the bore, Lenny conjectures that the salt-beds probably lie at a considerable depth in the coal, or in the upper strata of the silurian formations, as is the case at Syracuse, in the neighbouring State of New York, or at Abington, in Virginia. In both these places, however, gypsum is found. Lenny therefore starts the question whether, perhaps, in places where there are overlying coal-formations, the gypsum is separated from the brines by means of the baryta.\*

In order to show the possibility of brines being formed from sea-water deposits, whether these occur as pure rock-salt, or interspersed in sedimentary rocks, we shall endeavour to give an estimate of the average composition of the water of the sea. For this purpose the analyses of v. Bibra (p. 102), with the exception of No. XV, seem to be best adapted, inasmuch as the specimens of water examined by him were taken from parts of the ocean widely remote from one another. According to these, the medium composition of sea-water is as follows :—

\* It is not probable, although not impossible, that chloride of barium is present, as such, in rocks, or in rock-salt. From hepatic it is clear that sulphuret of barium occurs in the mineral kingdom (Chapt. I, No. 27), and this mineral may be chiefly found in coal-formations when, as in England and Scotland, sulphate of baryta is present in the same. Sulphuret of barium is decomposed by chloride of magnesium, as also by chloride of calcium : in this way chloride of barium is formed (No. 31 and 32). Both these chlorides occur in the above brines ; the conditions, therefore, are given by which the presence of the chloride of barium in the same may be explained. Together with the chloride of barium, however, sulphate of lime cannot occur. Since the latter salt is still more easily decomposed by carbonaceous substances than the sulphuret of barium, the percolating waters can have taken up only the gypsum, which is decomposed into sulphuret of calcium. In this case, however, the small quantity dissolved would, in contact with the air, have soon been converted into sulphate of lime. Such decompositions may be supposed to have taken place in the bore No. 1 the more easily on account of the presence of petroleum.



Saline contents	....	....	3·527
Chloride of sodium	....	....	75·786
Chloride of magnesium	....	....	9·159
Chloride of potassium	....	....	3·657
Bromide of sodium	....	....	1·184
Sulphate of lime	....	....	4·617
Sulphate of magnesia	....	....	5·597
			100·00

From the foregoing 48 analyses of brines occurring in different countries, and arising in different formations, we have the following results :—

1. The brines I, II, VI, VIII, XI, XIX, XXXI to XXXVIII, which contain the largest proportion of saline ingredients (11·1 to 26·39%) contain also the largest amount of chloride of sodium, (93·72 to 99·47%) : in those, on the other hand, in which the saline contents sink to from 10·53 to 0·82%, the chloride of sodium also diminishes to from 95·71 to 53·08%. It cannot, indeed, be set down as a general law, that the amount of saline constituents stands in direct relation with that of the chloride of sodium : in VIII, for example, the former is 11·1%, the latter being only 93·72% ; while in VII, the former is only 2·00%, the latter amounting to 95·71% ; it is, however, to be observed, that the chloride of sodium never approaches the maximum, when the amount of saline constituents approaches the minimum. The brines XXXI to XXXVII, which spring from rock-salt, contain the greatest amount of salts generally, and also the greatest proportion of chloride of sodium, as is the case in rock-salt itself. Since the weak brines, as we shall subsequently see, derive their saline constituents not from rock-salt itself, but from sedimentary rocks, and since, also, these brines, with few exceptions, contain more chloride of sodium, the richer they are in saline ingredients generally, we must conclude, that the amount of this salt present in these rocks is greater, the richer they are in salts generally. When pure rock-salt is, in the first instance, deposited from the sea, and afterwards becomes covered with earthy sediments, and when we find in its saline constituents a greater proportion of chloride of sodium than is contained in sea-water, the deposit of that rock-salt cannot have proceeded so far, that a mother-liquor remained, containing only little chloride of sodium, but a large quantity of the other sea-water salts ; on the contrary, even in this mother-liquor the chloride of sodium must still have predominated.

All this leads to the conclusion that, in most cases, subsequently to the deposition of pure rock-salt, this chemical deposition still continued even after the mechanical deposition of earthy particles had commenced, and that both went on simultaneously. If, however, the two deposits had always gone on together in the same sea-water, the chemical deposition of salts must have gradually diminished; suspended particles being, on the other hand, uninterruptedly carried into the sea, the saline constituents in the mechanical deposits must have steadily decreased. In this way is explained the circumstance so common in boring for rock-salt, that the chloride of sodium in brines always increases, the more nearly pure rock-salt is approached.

2. Among the 48 brines, there are only two (XLII and XLIV) in which the proportion of chloride of sodium is much less than in sea-water; in all the others, it is either far more or very nearly as much. These two brines, however, the former from its large proportion of sulphate of soda, the latter from the large quantity of chloride of calcium contained in it, exhibit a composition so abnormal, that the masses of salt from which their saline ingredients are extracted, must be supposed to have been formed under peculiar and rarely occurring relations.

3. Among the remaining 46 brines there are only two (XXIV and XLIV) in which the chloride of magnesium is present in greater proportion than in sea-water, in six (XXV, XXVII, XXVIII, XXXIX, XL, and XLVI) it amounts to nearly as much;\* in 14 it is altogether wanting, or present only in traces. Among these 14 brines there are seven which proceed from rock-salt, the remaining seven contain so small a quantity of salts generally, that they can only have extracted the same from rocks. Since, therefore, it is only in rare cases that the chloride of magnesium amounts to about as much or to more than is contained in sea-water, it follows that in most cases, neither in the rock-salt, nor even in the sedimentary formations covering the same, has it been left in the proportion in which it must have been present in a mother-liquor from which rock-salt had been deposited. This mother-liquor, therefore, either during the deposition of the earthy sediments in the sea, or after their elevation above its level, must

\* It is remarkable that XXIV, XXV, XXVII, and XXVIII, come from transition formations; and XLVI, as also XLVII and XLVIII, which in like manner contain much chloride of magnesium, from coal-formations. Whether this occurrence of brines which are very rich in chloride of magnesium, in the oldest sedimentary formations, be accidental or essential, must be determined by further researches.

have been displaced by the water which first percolated through them, and must have been again conveyed either immediately or mediately into the sea. During the first periods after the deposition of rock-salt in the different sedimentary formations, the chloride of sodium in the sea-water must, consequently, have always been diminished in much greater proportion than the chloride of magnesium.

However, as the analyses of brines and of river-waters show that chloride of sodium is now being, and has for a long time past been conveyed into the sea in much greater quantity than chloride of magnesium, the original proportion between the two chlorides in the sea-water must have been again nearly restored, and will be always more and more nearly approached.

The common salt, which is obtained by evaporating brines, contains, as is known, water mechanically: rock-salt does not. The former, therefore, must include mother-liquor, the latter not. This is evidently the reason why the common salt of salt-works contains far more chloride of magnesium than is found in rock-salt. The fact that rock-salt contains no such water, seems to show that its deposition from the sea has taken place very slowly.

4. Of the 46 brines there is only one (XVIII) in which the proportion of sulphate of magnesia is greater than in the sea-water; in 21 it is entirely wanting, and in the others it amounts to much less than in sea-water. Since large quantities of sulphate of magnesia are carried into the sea by rivers, (p. 82), since, moreover, according to the mean result of the analyses of river-water, the quantity so conveyed amounts to 1.57 more than that of the chloride of sodium and potassium, the percolating water must meet with more of the former than of the latter two salts in the mountain rocks. It is, consequently, to be supposed, that the mother-liquor which remained after the deposition of rock-salt, and with which the sedimentary deposits, subsequently formed, were saturated, was richer in sulphate of magnesia than in chloride of sodium. Whilst, therefore, sulphate of magnesia is, for the most part, entirely wanting in rock-salt, and in brines also is either absent, or occurs only in very small proportion, it must be present in those rocks from which no brines proceed, but from which salts are extracted by percolating water in much greater quantity than chloride of sodium. That, nevertheless, the sulphate of magnesia is in rare cases present in rock-salt itself in large quantities, we have already seen, and *bitter water* also indicates that it must be present in those layers from which such water proceeds.

Far more sulphate of magnesia than chloride of magnesium being carried into the sea by rivers, it follows, that in the sedimentary rocks which have been formed from the sea, the former salt has been left in much greater quantity than the latter. The sulphate of magnesia has become dry while the uncrystallisable chloride of magnesium may have been carried away in the mother-liquor.

5. Among the analyses of the brines there are nine in which the sulphate of lime is present in greater proportion than in the sea, and 35 in which it is less; in five it is quite wanting. Since this salt is the least soluble of the principal constituents of brines, it must amount to much less than chloride of magnesium, and sulphate of magnesia, when these salts are found together with chloride of sodium, in pure rock-salt, as well as in the rocks impregnated with it. This, however, as we have seen, takes place but seldom; and therefore in 26 brines the quantity of sulphate of lime exceeds that of both the magnesian salts together, and only in 17 brines is it less than the aggregate amount of these two salts. Since in sea-water, however, the chloride of magnesium and sulphate of magnesia are together three times greater than the sulphate of lime, this salt must in the majority of cases have been deposited in much greater proportion than the other two. What is shown by brines, is shown in a still higher degree by river-water; for the sulphate of lime in those rivers especially which empty themselves immediately into the sea, is, next to the carbonate of lime, the constituent which is present in the greatest abundance, and much exceeds the proportion of the magnesian salts.

Sulphate of lime is, therefore, carried into the sea by the rivers of the present day in greater quantity than any other salt, the carbonate of lime excepted. We must not lose sight of the fact of the consumption of the carbonate of lime in the formation of the shells of testaceous animals; according to Forchhammer, sulphate of lime is also applied to the same purpose. If this be the case, we can understand how this salt, although constantly conveyed into the sea, either does not increase at all or only in small proportion.

When the sea-water is concentrated by evaporation, its saturation point as regards sulphate of lime being reached sooner than as regards chloride of sodium, the deposition of the former salt must begin much earlier than that of the latter. This is also shown by the researches of Usiglio (p. 361); but according to these, during



the greater part of the evaporation the deposition of both salts goes on together. In thirteen specimens of rock-salt, we find also minute quantities of sulphate of lime, but in the other seven specimens no trace of it (p. 357 and 358). It appears, consequently, that during the crystallisation of the gypsum, it has been either entirely or, at least, for the greater part separated from the chloride of sodium. A similar separation is also seen in the case of druses of rock-salt occurring in gypsum, as in that at Artern.\*

Following the opinion that all rock-salt is a deposit from the sea, the floor of pure rock-salt layers must always be gypsum. But since the miner takes care not to break through the undermost and purest layers of rock-salt, and thereby allow the water to make its way into the pits, the composition of the floor is not known. The bores which have been made hitherto, however, have shown that before reaching the pure rock-salt, layers of gypsum or anhydrite must be passed through, and these in general contain the more chloride of sodium, the more nearly the rock-salt is approached.†

When, as in the bores mentioned in the preceding note, a frequent alternation between rock-salt and gypsum or anhydrite is met with, the gypsum which underlies each layer of rock-salt must be regarded as the first deposit, and the rock-salt as the second, that takes place from the same sea-water. From the same sea-water, however, after the deposition of gypsum and rock-salt in distinct layers has once taken place, gypsum cannot again be deposited. The gypsum which overlies the rock-salt must consequently proceed from a subsequent supply of sea-water. When we find, as is ordinarily the case, gypsum or anhydrite as the last deposit in a rock-salt formation, the sea-water from which these were

\* German edition, Vol 1, p. 206.

† At Buffleben, in Thuringia, and at Stotternheim, it is only after passing through gypsum layers  $157\frac{1}{2}$  and 169 feet in thickness, that rock-salt is reached. (Archiv. für Mineral., &c. Vol. 16, p. 552.) At Stebnick, in Gallicia, the bore passed through loam containing gypsum, then through loam containing a few small grains of salt, through a salt-layer two feet in thickness, through clay with gypsum, and at length arrived at pure rock-salt. In this way, seven different salt-layers, of greater or less thickness and purity, alternating with saliferous clay and sandstone, had been passed through. (Pusch, in Jahrbuch für Mineralogie, &c. 1845, p. 286.) Also the saliferous formations of Wieliczka consist of layers and large masses of salt which are separated by clay, marl, and anhydrite. (Zeuschner. Ibid. 1844, p. 527.) At Artern, rock-salt was first penetrated after passing through thick layers of gypsum: these were bored to a depth of  $87\frac{1}{2}$  feet without reaching the floor of rock-salt. (Poggendorff's Annal. Vol. 42, p. 583.) In the bore at Schöningen, at a depth of 1710 feet, pure rock-salt, and at 1721, anhydrite and gypsum were passed through; at the depth of 1819 feet, rock-salt with a little gypsum and anhydrite, again appeared. In the bore at Stassfurth the first traces of rock-salt appeared in anhydrite, at a depth of 792 feet. Since that time, 1000 feet of rock-salt have been bored, without reaching its floor.

separated must have flowed away before the deposition of chloride of sodium began.

The sea-water of the present day contains on an average 16·4 times as much chloride of sodium as sulphate of lime. From this, however, we cannot form even a proximate estimation of the relative proportions in which these two salts occur in saliferious rocks. When, however, we consider the thick layers of gypsum which must be passed through before pure rock-salt is reached, we cannot help thinking that the relative proportion between the chloride of sodium and sulphate of lime in rock-salt formations is not the same as in the sea. Circumstances must, therefore, have occurred which have given rise to the deposition of sulphate of lime in greater proportion than chloride of sodium. One principal cause undoubtedly depends upon the fact that the sulphate of lime in sea-water amounts to 0·63 of that contained in a saturated solution, while the chloride of sodium present in the same amounts to only 0·07 of the quantity occurring in a saturated solution. Consequently, when only  $37\frac{0}{100}$  of water is removed from the sea by evaporation, the deposition of gypsum already commences; whereas  $93\frac{0}{100}$  must be removed before the chloride of sodium can commence its deposit. The latter result agrees pretty accurately with that obtained by Usiglio.

6. No brines, in which the relative proportion of the other salts to the chloride of sodium is greater than it is in rock-salt, can be formed by mere solution of the latter. Such brines can only arise when the water which passes to the pure rock-salt layers, and becomes saturated with chloride of sodium, is diluted during its ascent to the surface by weak and impure brines, or when it does not reach the rock-salt at all, but extracts the saline ingredients from rocks which, like saliferous clay and gypsum, contain chloride of sodium. The brines from XXXI to XXXVII, in Würtemberg, come immediately from the rock-salt which has been bored; they contain at an average  $\frac{5}{7}$  of the entire amount of chloride of sodium which water can dissolve, and are consequently near the saturation-point. In their composition they approach very closely the rock-salt (VI, VII and VIII); they contain, however, more sulphate of lime (up to  $2\cdot27\frac{0}{100}$ ) than the latter. In their ascent they must, therefore, continue to dissolve this salt, which occurs in the anhydrite and saliferous clay which cover the pure rock-salt to the thickness of from 82 to 155 feet. Here, therefore, we have an instance of brine which arises in pure rock-salt still taking up saline substances during its ascent: for the brine XXXV must also still dissolve chloride

of calcium. I know of no observations which would enable us to determine whether their brines are thoroughly saturated with chloride of sodium at the depth where the pure rock-salt occurs, and then become diluted by water flowing into them during their ascent. If in other parts the saliferous clay contains, besides chloride of sodium, considerable quantities of other salts; as for example, chloride of magnesium, and if the brines which arise from the pure rock-salt, and are saturated to a greater or less extent with chloride of sodium, become mixed with more or less diluted solutions which derive their saline contents from the saliferous clay, impure brines may in this way come to the surface. In such a manner brines may arise which, like XXIV at Nauheim, contain as much as 12·6% of chloride of magnesium. Since, in this case, the brine proceeding from the pure rock-salt already contains chloride of sodium, the chloride of magnesium in the saliferous clay must amount to still more than is indicated by the analysis of the brine.

When the water does not penetrate so far as the pure rock-salt, but only to the saliferous clay and anhydrite, it must extract its saline contents only from them.

7. The rock-salt being almost everywhere surrounded with an impermeable covering of clay or anhydrite, there are very few brines which actually rise from the layers of pure rock-salt. The mining works in Sulz, Schwäbisch-Hall, at Salins, and other places, afford a clear illustration of this fact. Only where the rock-salt comes to the surface, as in Transylvania, the Marmorosch, in Algeria, upon Iluallaga, in Peru, &c., are the brines formed immediately from it.\*

The brines X and XI afford an opportunity of comparing a weak impure brine which was a long time ago employed for the preparation of salt, with an artificial almost saturated brine which is obtained from a bore in the rock-salt layers at no great distance from the other. The great quantity of foreign salts present in X, indicates that it can only proceed from the layers which cover the pure rock-salt. The composition of XI approaches that of the

\* This is the view of Alberti (*loc. cit.*, Vol. 1, p. 32) founded upon observations. From researches made upon the bores of Artern and Stassfurth, I had already (German edition, 1847, Vol. 1, p. 176) regarded it as probable that these brines are formed merely in the gypsum covering the rock-salt, and that water perhaps never, or only in exceedingly rare cases, penetrates as far as the rock-salt layers themselves. Afterwards, however (Vol. 2, p. 194), Alberti comes to regard it as undeniable, that the brines of Artern and Stassfurth come from rock-salt. To what inconsistencies does the spirit of contradiction lead !

pure rock-salt very closely. It is not, however, to be assumed that the chloride of magnesium, chloride of potassium, and sulphate of potash, which are present in no inconsiderable quantities, proceed from pure rock-salt; they are undoubtedly extracted from the layers which overlie it, by the brine during its ascent. The sulphate of lime may probably have the same origin; but it may also proceed in part from the gypsum which is often found in the druses of pure rock-salt. The brine X, according to observations made during a period of more than 20 years, has a constant temperature of  $57^{\circ}$  F. This temperature is attained in two neighbouring bores at the respective depths of 300 and 450 feet. At depths of 972 and 995 feet, where rock-salt was bored, the temperature of the brine was  $65^{\circ}\cdot 75$  to  $66^{\circ}$  F. From this we may judge approximately that the brine X comes from a depth of between 300 and 450 feet, which is from 545 to 672 feet above the pure rock-salt. Already, at a depth of 559 feet a brine was found somewhat stronger than it, and of a temperature about  $0^{\circ}\cdot 45$  F. higher. Beyond this depth the temperature rose pretty regularly,—the quantity of saline constituents, however, not so regularly. Still 4 feet above the rock-salt layers, the latter amounted to  $24\cdot 25\%$ , 1 foot deeper it rose to  $27\%$ —consequently nearly to the saturation-point. All these phenomena indicate that the brines proceeding from bores which do not reach the pure rock-salt, come, not from this, but from the gypsum which is impregnated with chloride of sodium. True saliferous clay was not met with in the bore at Artern, but still 468 feet above the pure rock-salt layers, while sinking a pit in gypsum, there was found a druse of rock-salt. There is, consequently, no doubt that water which does not penetrate nearly so far as the pure rock-salt layers, finds in the layers covering the same, a sufficient supply of salt; and that the brine-spring which was formerly employed at Artern for the preparation of salt has in like manner only such an origin.

Similar relations to those at Artern are also seen in the rock-salt bore at Staasfurth.

Thus far the conclusions founded upon the composition of the sea-water, of rock-salt, and of brines, lead us. We look around for facts which may open up the way still farther.

Wollaston,\* who examined samples of sea-water taken from the Mediterranean at different depths by Captain Smyth, obtained the following results :

\* Phil. Trans. 1829. Part 1, p. 29.



Distance from Gibraltar.	Depth.	Sp. Gr.	Proportion of salts in 100 parts of water.
Eng. miles.	Feet.		
680	2,700	1·0294	4·05
450	2,400	1·0295	3·99
50	4,020	1·1288	17·3

He concludes from this, that an under-current of denser water again carries back to the Atlantic the salt which the upper current has brought into the Mediterranean.

Macmichael found no difference in the specific gravity of the water at the surface of the Mediterranean and that at a depth of 1500 feet; an observation which agrees with those of Wollaston. Liston, on the contrary, found in the Sea of Marmora—

Latitude.	Longitude.	Sp. Gr.	Depth.
40° 30'	26° 12'	1·0294	204 feet
40 30	26 12	1·0215	Surface
41 00	29 00	1·0157	180 feet
41 00	29 00	1·0145	Surface

from which we might conclude that the proportion of saline constituents increases with the depth. According to Marsigli and Wilke also, the deeper strata of the water of this sea are much richer in salts than those nearer the surface, which was confirmed by the researches of Marcet. This difference may, however, depend upon the currents of lighter water which come from the Black Sea.\*

Against the accuracy of the researches of so distinguished and scientific an observer as Wollaston was, nothing certainly can be said.† But there are still other phenomena which show that in a

\* Physikal. Wörterbuch. Neue Bearbeitung. Vol. 6, p. 1631 and 1644.

† Muncke (Ibid, p. 1771), however, raises doubts against these results, Although I cannot participate in these, still I hold a repetition of the researches,

column of water the particles which have become impregnated with salt in the upper parts sink, and that even in a column of salt-water there is an upper or weaker saline solution, and a lower or stronger one. This phenomenon is exhibited in the pits sunk in saliferous clay for the purpose of dissolving the chloride of sodium. The water, which is conducted into them, dissolves scarcely anything at the bottom, very little at the walls, but a large amount at the surface. The particles of water which have here become impregnated with salt sink through the lighter water, while this comes continually into contact with the saliferous clay. In bores which are filled with brine, a reverse phenomenon is observed; an increase of the saline contents with the depth. In this way it was found in the bore at Artern, after the operations were finished, that in a state of repose the amount of saline ingredients was, towards the surface 4.5%, at the depth of 996 feet, on the other hand, 27.4%.

At Dürrenberg also, however, where no rock-salt was reached, it was found, after the boring operations had ceased, that the quantity of saline ingredients in the brine of the pits increased regularly. At a depth of 50 feet they amounted to 5.467%, and at a depth of 1035 feet to 17.345%. In order to ascertain the influence of the sinking of the saline particles of a column of brine in a state of repose, an iron tube, 25 feet high and  $3\frac{1}{2}$  inches wide, was filled with Dürrenberg brine containing 8.836% of solids, and its upper extremity secured with bladder. After eight months, more than one half of the fluid was lost from some unknown accident. Notwithstanding, it was found that the saline contents were at the surface 1.416%, while, quite at the bottom of the tube, on the other hand, they amounted to 14.703%.\* There can, therefore, be no doubt that in a column of brine in a state of repose the saline particles gradually sink towards the bottom.†

Since this is an object of great geological interest, further researches appeared to me not superfluous.

I. Into a perpendicular tube,  $8\frac{1}{2}$  feet high, filled with water, I allowed a saturated solution of common salt to filter along the

considering the importance of the object to which they refer, as much to be desired. I have therefore expressed this wish to Sir. Ch. Lyell, and he has had the goodness to request Sir William Reid, Governor of Malta, to obtain water from different depths of the Mediterranean Sea for chemical examination. I shall perhaps be able to communicate the results of the same in an Appendix to the present work.

\* German edition. Vol. 1, pp. 175 and 211.

† The diminution of temperature in proportion to the depth, in lakes and in the sea, shows that currents take place in them from above downwards, indicat-

inclined surface of a funnel. The solution flowed slowly in a very thin layer along the walls of the tube into the water, and had time to become mixed with the same, but not to sink through it.

After  $2\frac{1}{2}$  hours the salt contained in the tube was—

		Above	Below
		0.304%	0.176%
After 5 days	....	0.191	0.211

Within the  $2\frac{1}{2}$  hours, therefore, most of the saturated solution was still accumulated in the upper part. After five days, however, the greater part of it had sunk, and there was an increase of the saline contents from above downwards of about one-tenth.

II. A perpendicular tube of lead, open above and closed at its lower extremity,  $19\frac{1}{4}$  feet in height, and with a bore of one inch in diameter, was filled with a solution of common salt. After a period of three weeks no marked difference was observed between the saline contents in the upper and lower parts.

III. The same tube was filled with distilled water, and a glass tube, filled with common salt, and secured at its lower end with linen cloth, was suspended in it. The leaden tube was corked to prevent evaporation. Only after four days was the salt fully dissolved. The saline contents were equal in the upper and lower parts of the tube, which was also the case two days later. After the tube had been allowed to stand eight months undisturbed, there were—

	Above.	In the middle.	Below.
	1.286%	—	1.318%
Three days later,	1.294	1.307%	1.309

The concentrated solution formed by the dissolving of the

ing naturally currents in the opposite direction. (My Physical, Chemical, and Geological Researches on the Internal Heat of the Globe. London, 1841, p. 102.) Researches which I have instituted (Die Wärmelehre des Inneren unsers Erdkörpers. 1837, p. 429) show that the slightest increase of the specific gravity of water at the surface, caused by a decrease of temperature, is alone sufficient to originate descending currents. Evaporation, and as a consequence of the same concentration of the saline contents, also effect this in the same manner as decrease of temperature. The sinking of the particles of water which have in this way become specifically heavier, takes place more rapidly than the mixture with the neighbouring particles; consequently, the former pass downwards through the latter. Should both actions, diminution of temperature and evaporation, combine to produce an increase of the specific gravity, the sinking of the particles of water will be the more facilitated. The increase of the specific gravity of sea-water, in consequence of the decrease of temperature, amounts to 0.001 for every  $18^{\circ}$  F. Since now a much slighter diminution of temperature causes descending currents, it may be seen how little the water at the surface requires to be evaporated in order to give rise in like manner to such currents.

common salt had, therefore, sunk within three days, and had become so mixed with the water that a solution of equal strength throughout was the result. Subsequently, however, a separation took place; a stronger solution collected below, and after eight months a difference of 0.032 was exhibited between the upper and lower portions of the fluid contained in the tube. That three days later this difference should have diminished to 0.015%, could only have depended upon the circumstance, that a motion must have been produced in the fluid while taking out the specimens for chemical examination, and in this way a partial mixture of the solutions at different heights have taken place.\* It is proved, however, by these experiments, that in a column of saline solution of equal strength, standing at rest, a separation after a long time takes place, by which a stronger solution sinks towards the bottom. It deserves particular attention, that this separation still took place in a solution which contained only 1.3% of salt. In like manner, by the first experiment it is shown, that a concentrated solution of salt, if it flows pretty quickly into a column of pure water, sinks too rapidly to allow a perfect mixture with the water to take place.

From observations which I made, I have ascertained that at the foot of a column of water of considerable height (the tube was 6 feet high), the variation of temperature, when the external temperature varies about 9° F., amounts to only 2° F., at the upper part, on the other hand to 3.6° F. When the external temperature rises, therefore, ascending water-currents take place; when it falls, currents in the opposite direction ensue.† In the leaden tube already mentioned, which had stood in the laboratory from the 8th of March to the 8th of November, such currents must, in consequence of the frequent changes of external temperature, have been of almost daily occurrence. They must have exercised an influence opposed to the separation of the fluid into stronger and weaker solution. Could they have been prevented, a much greater difference would no doubt have been observed between the saline contents in the upper and lower parts of the tube.

By evaporation the water at the surface of a sea must become concentrated. Were a sea a column of water in a state of rest, it would present a progressive increase of its saline constituents from the surface downwards, as is observed in the bores

\* The salt, as was to be expected, had not acted on the lead; the sulphuretted hydrogen passed through the solutions did not give rise to the slightest turbidity.

† Die Wärmelehre des Innern unsers Erdkörpers. 1837, p. 438.



already mentioned. So far down, however, as the movements of the waves extend,\* the particles of water are mingled together; thus far, therefore, the proportion of saline constituents is equal. If, however, that should be increased ever so little, in consequence of evaporation, the water which has become specifically heavier will, as in the case of the bores, sink beneath the specifically lighter water of the tranquil sea. This is sufficient to explain the greater proportion of saline constituents in the lower strata of the waters of the Mediterranean.

This phenomenon is, however, intimately connected with the circumstance, that the sea in question receives less water through the medium of rivers and rain than it loses by evaporation. Since it is richer in saline ingredients than any other sea the waters of which have been as yet analysed, whether that be the ocean itself, or a sea communicating with the same, there can be no doubt that what has just been stated really takes place. In regard to the current which flows from the Atlantic into the Mediterranean, Smyth shows that the central current runs constantly at the rate of from three to six miles an hour eastward into the Mediterranean, the body of water being three miles and a half wide. Vessels which have sunk in the Straits of Gibraltar and again appeared in the Atlantic,† indicate the existence of an under-current passing in the opposite direction. It appears, however, from Captain Smyth's soundings, that between the Capes of Trafalgar and Spartel, which are 22 miles apart, and where the Straits are most shallow, the deepest part, which is on the side of Cape Spartel, is only 1320 feet. It is, therefore, evident, Lyell remarks,‡ that if water sinks in certain parts of the Mediterranean, in consequence of the increase of its specific gravity, to greater depths than 1320 feet, it can never flow out again into the Atlantic, since it must be stopped by the submarine barrier which crosses the shallowest part of the Straits of Gibraltar.

In the ocean the relations are different. If the particles of water at its surface become concentrated and sink, such water, rich in saline constituents, must still, by means of currents, be con-

\* This depth seems to correspond with that at which animals are still found growing with one extremity attached to the bottom of the sea, and whose nourishment is brought within reach by the movements in question. Both depths do not seem to be much more than 600 feet. Elie de Beaumont in *Annal. de Chim. et Phys.* Ser. III, Vol. 2, p. 118.

† *Phil. Trans.*, No. 385, p. 191. *Gilbert's Annal.* Vol. 68, p. 139.

‡ *Principles of Geology.* London. 1833. Vol. 1, p. 297. *Elements of Geology*, latest edition, pp. 295, 296, &c.

stantly mingling with water containing a small quantity of them, and in this way cannot collect in any one place. Moreover, the ocean, taken in its whole extent, is always receiving as much water from rivers, as well as by means of rain and snow, as it loses by evaporation. A distinct increase in the amount of saline constituents with the depth has not been shown by any of the researches which have yet been made (p. 97). Water taken by Lenz from a depth of 6000 feet, consequently 2000 feet greater than that from which the specimens collected by Captain Smyth were taken, showed nevertheless no increase in the specific gravity.

Only in inland seas, or at least in such as merely communicate with the ocean by narrow channels, and which, therefore, take no part in the great currents affecting the latter, can an increase in the saline constituents in proportion to the depth take place, in consequence of the causes above-mentioned. That such a partial increase cannot give rise to a general decrease in the saline contents of the ocean is easily seen, when it is considered that the water conveyed to it by rivers is not pure, but contains salt, although in small quantity (p. 82).

By the continuance of the evaporation in the Mediterranean, Lyell remarks,\* additional supplies of brine are annually carried to deep repositories, until the lower strata of water are fully saturated, and precipitation of continuous masses of pure rock-salt, extending perhaps for hundreds of miles in length, takes place. In reference to this, it must be observed, that even if by evaporation the surface water should become quite saturated with salt, this saturated fluid cannot reach the deeper parts, quite unmixed with water poorer in salt. Even if no wave-motion took place, such an inter-mixing would still result, and more so if the sea be in violent agitation. At present, therefore, certainly no rock salt is deposited upon the bottom of the Mediterranean, nor does this appear to be Lyell's opinion. Were its saline ingredients to be augmented until the proportion  $17\frac{3}{8}\%$ , at present found at a depth of 4020, came to be that contained in the water at higher and higher levels, and finally in that at the surface, they would still admit of further increase. So long, however, as it continues to receive supplies of fresh water through the medium of rivers and rain, and sea-water from the Atlantic, it will scarcely be brought into a state of complete saturation.

Should the communication between the Mediterranean and the Atlantic be by any accident interrupted, and thereby the supply of

\* Principles of Geology London, 1833, p. 298.

water from the latter cut off, the relations would be quite altered; the quantity of water removed by evaporation would then outweigh that which streams into it from the rivers, the whole sea would be brought to the condition of a saturated solution, and the precipitation of rock-salt necessitated. In the Dead Sea such has, perhaps, already taken place.

Could it be shewn that rock-salt always occurs in basins, the margins of which are formed by old rocks, such basins might be compared with formerly existing bays of great extent, containing large quantities of sea-water which was gradually evaporated, its saline ingredients remaining. It might, however, be difficult to find in every case such margins surrounding the layers of rock salt; the extensive layers at Würtemberg, Baden, and the Grand Duchy of Hesse, for example, have none such.

The manner in which beds of salt are at present deposited from sea-water is seen on the Bessarabian coasts of the Black Sea. From the mouth of the Danube, as far as the Nieper, all the rivers before terminating in the sea expand into lakes (limans) of greater or less extent, which are separated from the sea by natural dams. The water flows into the sea through an opening in the dam, while, on the other hand, during storms, sea-water flows into these limans. In the water of the extensive limans which are formed by the larger rivers, as the Nieper, Niester, &c., and which receive a large volume of fresh water, the proportion of salt is so small as not to be perceptible to the taste. The three Bessarabian limans, however, situated to the south-west of Odessa, become partially dry every summer, and deposit their salt in crystals, which in the neighbourhood of the shore are of small size and form beds only  $\frac{1}{2}$  to 1 inch in thickness, but in the middle of these limans the crystals are larger and often form beds 1 foot in thickness. This salt is employed for commercial purposes, and it is stated\* that in the year 1826 more than 6 million pud (216 million pounds) were obtained. That such deposits took place during the præhistoric periods there is no reason to doubt. If we imagine a continued sinking of the coasts and bed of such a liman, we have a picture of a rock-salt formation on no small scale. One of the limans measures more than 40 English miles in length and 2 to 3 wersts in breadth.

The water of the Dead Sea, which is 60 English miles in length and 15 in breadth, the composition of which has been stated (p. 92), can only be regarded as a mother-liquor formed by the evaporation

\* I. G. Kohl. Reisen in Süd-Russland. Vols. 1 and 2. 1841.

of sea-water or of other water containing salt. The relatively large quantity of bromide of magnesium present in it, also leads to the conclusion that a long-continued process of evaporation has taken place; for such quantities of this bromide occur only in concentrated mother-liquors from which much salt has been deposited. Inasmuch as this sea is always receiving water but has no visible outlet; and since, on account of the low level at which it is situated, there can be no subterranean way of escape, the waters conveyed into it can only be again removed by evaporation, and must therefore leave their saline ingredients behind.

The waters of this sea are subject to a considerable rise and fall during the year. The rains of winter and the melted snows of Mount Libanon produce a rise of several feet, while the long-continued heat of summer being very intense, produces an abundant evaporation. Robinson and Smith saw decided evidence in the driftwood lodged along the shore, that the waters had been, during some part of the year, as many as 15 feet higher than when they visited them. This, of course, produces a considerable difference in the superficial extent of the sea at different times. The valley extending southerly, is for several miles very low; so that, in fact, a rise of the waters a few feet causes them to extend southerly several miles.\*

This large increase in the superficial extent of the Dead Sea certainly favours evaporation very much; yet such an evaporation in a warm climate is greater than we are commonly accustomed to suppose.†

The water of the Jordan, the chief river which flows into the Dead Sea, consists, according to Hermbstädt's‡ analysis, of—

Chloride of sodium	....	....	....	0.35
"    of magnesium	....	....	....	0.03
"    of calcium	....	....	....	0.07
Sulphate of lime	....	....	....	0.04
Water	....	....	....	99.50
				99.99

This river, therefore, contains 12 times as much chloride of sodium

\* Notes on the geology of several parts of Western Asia, founded chiefly on specimens and descriptions from American Missionaries, by Edward Hitchcock, in Reports of the meetings of the Association of American Geologists. Boston. 1843, p. 369.

† At Port Louis, in the Mauritius, the evaporation amounted to—  
in the year 1841, 4 feet, 6 inches, 7-10ths

    "    1842, 4 " 4 " 2-10ths  
Poggendorff's Annal. Vol. 61, p. 414. Although this evaporation is very great, it is still considerably exceeded by that of the Dead Sea.

‡ Schweigger's Journ. Vol. 34, p. 183.



as chloride of magnesium, while in the water of the Dead Sea the former amounts to only  $\frac{7}{12}$  of the latter :—of the 0·35% of chloride of sodium in the Jordan, 0·3325% must consequently be deposited in order to give the relative proportion in which the two chlorides are present in the Dead Sea.\* Hitchcock endeavoured to show that the hot springs on the west shore of Lake Tiberias, the waters of which have an excessively salt and bitter taste, are the principal source of the peculiar qualities of the water of the Dead Sea.

The shores of the Dead Sea are loaded with salt. On its south-west side there exists an interesting deposit of rock salt called Kashum Usdum. It forms a ridge from 100 to 150 feet high, and 5 miles long, covered in many places with layers of chalky limestone. This fact seems, according to Hitchcock, to settle its place among the formations; proving it to be connected with the cretaceous group. He found in it distinct traces of a sulphate as well of lime and magnesia, but could not detect either bromine or iodine. Usdum, therefore, cannot be the principal origin of the salts contained in the Dead Sea, for then common salt would be the chief ingredient; yet, doubtless, it increases the quantity of that substance, and the brackish springs along the shore have some effect. According to Bertou† the salt streams proceeding from the hills of the Valley of Waddi, el Chlor, constitute the chief sources of the large amount of saline ingredients contained in this sea.

Should the supplies derived from all these sources contain more chloride of magnesium than chloride of sodium, they would still scarcely counterbalance the larger amount of the latter than of the former brought by the Jordan, inasmuch as the volume of its water greatly exceeds that of the water of all these.

According to Strabo's narrative, the Dead Sea occupies the site on which formerly stood the cities of Sodom and Gomorrah, which were destroyed by a violent earthquake attended by a fiery eruption (or in the words of the Bible, by a shower of brimstone). According to the observations of Russegger,‡ the whole valley of the Jordan is an extensive cleft, formed probably by volcanic agencies. Hitchcock, on the contrary, draws from the researches of the missionaries the conclusion, that there is no evidence of any proper volcanic eruption having taken place in or around the Dead

\* In accordance with Hermbstädt's observations, Hitchcock (*Ibid.*, p. 371) found by examination in test-tubes, that the sulphates were evidently in much greater quantity in the water of the Jordan than in that of the Dead Sea; but the magnesia was most abundant in the latter.

† *Bulletin de la Société de Géographie.* 1839. Vol. 10, p. 274.

‡ *Poggendorff's Ann.* Vol. 53, p. 182.

Sea. Craters and lava may yet be found in the mountains east of the sea; but if the sea itself formed the crater, it is incredible that the lava should not be found covering the western shore.

Bertou, and particularly Letronne, have brought forward arguments to show that the basins of the Dead and Red Seas have been from the first distinct from one another. Russegger, on the other hand, regards it as possible that both seas once were in communication, and that they were separated from one another for the first time by the elevation of the ridge between the Waddi-el-Chlor and the Waddi-el-Araba.

If Russegger's view be correct, the water of the Dead Sea may be regarded as a mother-liquor, which has been formed by the evaporation of sea-water. Its surface being situated from 1314 to 1341 feet below that of the Mediterranean,\* a column of water equal to the difference in level between the two seas must have been removed by evaporation; since, meanwhile, all the land in the neighbourhood of the Dead Sea must have been covered to the same level with sea-water, a volume of water must have been evaporated which reached as far as the Lake of Tiberias, a little over 60 miles distant from the Dead Sea; for that lake is, according to Seymond, also situated 84 feet below the level of the Mediterranean. By the concentration of so great a mass of water, and consequent separation of common salt, a mother-liquor might well have arisen such as the waters of the Dead Sea represent. Ehrenberg,† however, finding in the water, as well as in the substances taken from the bed of this sea, fresh-water organisms for the most part still alive and capable of reproduction, concludes that it is a brackish fresh-water lake which has never been in direct communication with the sea, the small organisms present in the latter being in the Dead Sea either entirely wanting, or represented only to a very small extent.

Against this view, however, there are a few remarks which may be made. The shore of the Dead Sea consists of chalky limestone. All round, and especially in the valley of the Jordan, the limestone formations extend for unknown distances; this river, as well as the other waters which flow into the Dead Sea, are, therefore, daily conveying thither carbonate of lime in solution. In spring, during the melting of the snow, or after heavy rains, if the waters become turbid, they must bring large additional quantities of the

\* Poggendorff's *Annal. Ergänzungsband*. 1840, p. 356; and Seymond, in *Compt. rend.* Vol. 20, p. 884.

† *Jahrbuch für Mineralogie*. 1850, p. 489.

same substance in suspension. All this earthy matter remains in the Dead Sea. Nevertheless, in this water carbonate of lime was not found by the analyses. Therefore, not only are the suspended particles of carbonate of lime deposited, but likewise that held in solution. Ehrenberg found that the mud taken from the bottom of this sea effervesced strongly with acids, and contained, as shown by the microscope, a large number of polythalamia. There is, consequently, no question that the bed of the Dead Sea must be covered with thick sediments. Had it, therefore, at any time stood in communication with the ocean, the then-existing marine organisms would have been buried long ago beneath these deposits, and can, on this account, no longer be found. Hence the occurrence of fresh-water forms in the Dead Sea cannot be regarded as a proof against its having formerly been in direct communication with the ocean.

So long as no source is found from which the Dead Sea could have derived much chloride of magnesium, and, at the same time, little or no chloride of sodium, the composition of its waters can only be explained on the supposition that the latter salt has been deposited in large quantity. No such source can be imagined, since neither the beds of rock-salt nor the sea-water contains more chloride of magnesium than chloride of sodium; on the contrary, the former salt is in these either quite wanting, or exists in only very small proportion compared with the latter. Had the salt-water of the Dead Sea been formed by the evaporation of that of the Mediterranean, thirteen times as much common salt must have been deposited as is at present contained in it. In this case thirty-seven times the volume of the water now existing in it must have been evaporated. The supposition that the water of the Dead Sea had from the first the same composition which it has at present, is altogether improbable.

The common salt which has been, and still continues to be, deposited upon the bottom of the Dead Sea, is precipitated simultaneously with the carbonate of lime which is held in solution by its waters. These chemical deposits are intermingled with particles of clay, the saliferous formations in the neighbourhood being also covered with layers of marl. In spring, when the streams are turbid with the particles of carbonate of lime and clay, mere mechanical deposits take place; for at this period, when large masses of water are carried into the Dead Sea, and the saline solution thereby diluted, while at the same time the evaporation is but slight, no common salt is deposited. During the ensuing

warmer months, the chemical deposition of common salt and carbonate of lime takes place. Should the streams become turbid at this season in consequence of continued rain, deposits are formed which contain a less amount of common salt. In this way there must arise a constant alternation of different irregular layers of greater or less thickness. All these layers must contain gypsum, since, in a water which contains so much chloride of magnesium as is present in the Dead Sea, gypsum, as we shall subsequently see, is dissolved with difficulty, as is also shown by the small proportion in which this salt exists in that sea. All the sulphate of lime, therefore, which is carried into the Dead Sea must be deposited.

These deposits upon the bottom of the Dead Sea present a true picture of the mode of origin of those formations which, like saliferous clay, consist of rock-salt, associated with sedimentary masses. The thick salt-stock at Hall in the Tyrol, which consists entirely of irregularly mixed precipitates,\* is an example of such a formation. At Dürrenberg, near Hallein, the clay is often traversed in all directions by thin layers of rock-salt and gypsum, frequently not above a line in thickness.†

Three saliferous clays in Berchtesgaden differ, according to Schafhäutl,‡ from the ordinary kinds of clay, in containing a large quantity of carbonate of magnesia and some sulphuret of iron. The finely pulverised mineral, after being first freed from common salt and gypsum, by washing with water, effervesced when treated with acids. The soluble constituents consisted of chlorides of sodium and magnesium, and sulphate of lime: the insoluble were as follows:—

	I.	II.	III.
Silica ....	47·75	53·00	6·45
Alumina ..	12·90	17·10	4·80
Carbonate of lime....	4·85	1·85	42·40
"    of magnesia	14·45	12·33	40·60
"    of iron	16·81	14·55	0·90
Bitumen .....	2·53	1·18	4·31
Water .....	0·68	.....	.....
Sulphur .....	.....	.....	0·51
	99·97	100·01	99·97

\* Kopf, in Karsten und v. Dechen's Archiv. für Mineralogie, &c. Vol. 15, p. 425.

† Schroll, in v. Moll's Jahrbüchern der Berg und Hüttenkunde, Vol. 1, p. 199.

‡ Münchener gelehrte Anzeigen. 1849. No. 183.



I. Light-grey saliferous clay, which occupies the spaces between the brown salt crystals.

II. Darker sort.

III. Blackish-brown saliferous clay; emits a bituminous odour when broken, and evolves sulphuretted hydrogen when treated with hydrochloric acid.

The deposition of similar saliferous clays, though not containing so large a proportion of carbonate of magnesia, the presence of which in such quantity is very remarkable, might well be conceived to take place in the Dead Sea. Were this sea once filled with sediment, a mighty formation of this kind would be the result.

Marchand\* found in an earth from the salt-desert, Zeph, situated to the west of the Dead Sea, 16% of soluble salts, and among these a large amount of bromide of magnesium. It is in the highest degree probable that this saliferous earth is a deposit from the Dead Sea, which has here become dry, inasmuch as the valley, as we have already seen, is for several miles very low, and a large quantity of bromide of magnesium can only be deposited when a mother-liquor, like the water of the Dead Sea, is dried in upon the soil.

In such narratives of journies as I have read, I nowhere find mention made of deposits of common salt upon the bed of the Dead Sea. In regard to what occurs in the deeper parts of this sea, we know nothing.†

The solubility of chloride of sodium in water diminishes, the greater the amount of chloride of magnesium therein dissolved. Water, containing 27·4% of chloride of magnesium, dissolves only about 1% of chloride of sodium. The more, therefore, the chloride of magnesium becomes concentrated by the evaporation of a brine-spring or of a sea-water, the more rapidly is the chloride of sodium deposited. According to 18 analyses of mother-liquors, which were obtained by evaporating the brines from I to XVII, at the salt-works of these places,‡ the chloride of magnesium and chloride of sodium, taken together, amounted to from 22·1 to 28·8%. Since, however, some chloride of sodium had been deposited from most of the specimens examined, which was again dissolved in warming the mother-liquor, the maximum given above would not have been so great had the deposited salt been deducted. The sum of the

\* Poggendorff's Ann. Vol. 76, p. 463.

† Moore and Beck found the sea 1,800 feet deep in some parts. Journ. of the Geographical Society. Vol. 7, p. 456.

‡ Heine, loc. cit.

chlorides of sodium and magnesium seems, therefore, to be always nearly the same, the number 22·1% representing it pretty closely. This is the more to be expected, since the sulphates, present in greater or smaller quantity in the mother-liquor, affect the relative solubility of the chlorides of sodium and magnesium. The solubility of the chloride of sodium, as also of chloride of potassium, is diminished by chloride of calcium, almost in the same proportion as by chloride of magnesium. In two of the mother-liquors, examined by Heine, in which these four chlorides were present, their aggregate amount was 29·5 to 29·9%.

In the Dead Sea, the four chlorides in question amount, together, to 21·4 or 26·2%. The water of this sea, therefore, inasmuch as it contains a large quantity of earthy chlorides, must be saturated with common salt; and since the latter is constantly being carried into it by the Jordan and the other streams, it must be as constantly deposited. This is also very strikingly seen, by comparing the analyses of the water of the Dead Sea, I, II, and IV, with III. In the water analysed by Klaproth,\* there was a cubical crystal, undoubtedly common salt. Since the water of this sea is, even at the surface, a saturated solution corresponding to the mother-liquors of salt works, we cannot expect an increase of its saline constituents with the depth. All these circumstances, therefore, lead to the conclusion, that in the Dead Sea a deposition of common salt is taking place, in consequence of the evaporation of the water. In the Dead Sea, therefore, we have the formation of rock-salt beds going on before our eyes.

The lake of Oroomiah, in the north-west of Persia, eighty miles long, and in some places thirty miles broad, is also a salt-lake. Next to the Dead Sea, its waters are more highly impregnated with salts than any that have yet been analyzed. Like the Dead Sea, it has no outlet; but instead of being depressed below the level of the Ocean, like that sea, it is probably not far from four thousand feet above the level of the Black Sea. Only a few small streams flow into the lake. The specific gravity of its water is 1·155; the composition—

\* Beiträge zur chemischen Kenntniss der Mineralkörper. Vol. 5, p. 185. Klaproth found 7·8 chloride of sodium, 24·2 chloride of magnesium, and 10·6 chloride of calcium. These two different salts could not possibly, however, have amounted to so much; otherwise, as Heine's researches show, 7·8 chloride of sodium could not have been present. From the tenour of his analysis, it appears that he has not determined the chlorides of magnesium and calcium in the anhydrous state.

Chloride of sodium	....	....	19.05	92.70
” of magnesium	....	....	0.52	2.53
Sulphate of lime	....	....	0.18	0.88
” of magnesia	....	....	0.80	3.89
Water	....	....	79.45	.....
			100.00*	100.00

The composition of this salt-water is quite different from that of the water of the Dead Sea. Since in the former, the chloride of magnesium amounts to only a very little, a much greater quantity of chloride of sodium may be dissolved by it than by the latter. The proportions of the different ingredients, as indicated by the second range of numbers, are very different from those in pure rock-salt, consequently the lake of Oroomiah cannot be regarded as a mere solution of pure rock-salt.†

The water of the lake rises every spring, three to five or six feet during the annual freshets from rains and the melting of snows on the surrounding mountains: and as these cease, the lake gradually subsides to its summer level. In most places, the land in its neighbourhood is flat, and raised but a few feet above the ordinary surface of the water. It is, therefore, extensively overflowed in spring; and as the waters of the lake gradually subside, a very thin incrustation of salt is left on the land thus overflowed. A bishop, who lives on the shore of the lake, stated that salt-banks exist, the surface of which was usually covered with a layer of sand; and that, in penetrating into them, you would pass through alternate layers of salt, and of sand or earth. Here, then, we have relations presented, such as may with good ground be conjectured to exist on the bottom of the Dead Sea.

Whence comes the extreme saltiness of this lake? A few facts will, according to Hitchcock, give a satisfactory reply to this

\* Hitchcock, loc. cit., p. 404. This chemist gave, according to the view of Marcet, chlorides of magnesium and calcium and sulphate of soda as constituents. I have, however, reduced these salts to chloride of sodium, sulphate of lime, and sulphate of magnesia.

† Dr. Marcet, who long previously analysed the water of this lake, but had limited himself to the determination of the magnesia, of the chlorine and sulphuric acid, found seven times as much of this acid as was found by Hitchcock. The latter, therefore, observes that when he first received the water it was so strongly impregnated with sulphuretted hydrogen as to tarnish silver at once. Could this gas have resulted from the decomposition of the sulphate in the water? If so, as nothing of the kind is mentioned by Dr. Marcet, it may explain the smaller quantity of sulphates found by Hitchcock. Again, the specimen he analysed was taken from the north end of the lake, and it may be that Dr. Marcet's specimen was obtained from some other part, where springs abounding in sulphates empty into the lake.

question. In the first place, the country to the east and north of the lake contains some of the most remarkable deposits of rock-salt in the world. Large beds of it occur near Tabreez, in Red Mountain: and from that mountain there comes down a stream, several rods wide, of salt-water which runs into the lake: it is not so salt as the water of the lake, but too salt for comfortable use, though the natives do use it. This mountain is about forty miles from the lake; but a salt-plain extends from thence to the lake. Another bed of rock-salt at Khoy is only eight or ten miles from the north end of the lake; we have then an abundant source of the salt in its waters. So far as lithological specimens can go, the probability is strong, according to Hitchcock, that this formation is the new red sandstone.

He examined some specimens of rock-salt from these deposits. One of these was the purest salt he had ever met with. Another was as limpid as rock-crystal: he could not detect a trace of sulphate of lime or of magnesia. For this reason, he considers that the other salts in the Lake Oroomiah are derived from the mineral springs in its vicinity.

That these springs contribute somewhat to them is certain, but the most part of the accumulation of these other salts in the salt-lake depends undoubtedly on the gradual deposition of common salt upon its banks, in consequence of the evaporation of the waters flowing out of it. The mother-liquor, which contains a portion of the uncrystallizable salts, and also a smaller portion of the crystallizable, flows back into the lake, and here accumulates.

In the vast low plain of northern Asia, in the most depressed part of which are situated the Caspian and Aral Seas, and which stretches far into the interior, extending beyond Sarepta to the Elton lake, and into the steppes of Bogdo, between the Wolga and the Iack there are numerous brine-pools. They lie lower than the Ocean, or on a level with it.\* In the Government of Astrachan, 129 such pools, only 32 of which are at present turned to use, are known. Around Kistiar, in the region of the Caucasus, there are 21 pools, 18 of which are used. They are round or elliptical in shape: their circumference seldom measures more than 9,000 to 12,000 feet. The whole soil along the shores of the Caspian sea, from the Wolga to the Terek, is so strongly impregnated with salt, that only a few salt-plants grow in it.†

\* Von Humboldt. *Asie Centrale*. Vol. 1, p. 49.

† Poggendorff's *Annal*. Vol. 17, p. 505. On the origin of the salt of the Steppe of Astracan, consult Murchison, &c. *Loc. cit.*, pp. 196 and 320.



The saline contents of all these brine-pools are, as in the case of the Dead Sea and Lake of Oroomiah, derived from streams impregnated with salt. These again derive this from beds of rock-salt or from saliferous soil. Only two rock-salt formations are known to exist in the Russian dominions;\* the one at Ilel,† the other at the Tschaptschatschi.‡ The former is covered by a sand-bed, which varies in thickness from a few feet to several fathoms, according to the inequality of the undulating surface. In the Tschaptschatschi, the rock-salt presents itself as large masses in different hills. The small depth at which the salt-beds of Ilel lie, explains how the rivers and brooks, which flow into the salt-lakes, may so easily intersect such beds, and extract therefrom the salt they contain. The soil in these regions, however, being, as at Irtysh,§ highly impregnated with salt, since also the whole steppe between the Ural river and the Wolga also contains a great quantity of this substance, it may be more from the salt contained in the soil, than from true salt-beds, that these rivers derive their supplies.

According to G. Rose,¶ the brine-pools of Russia have always deposits of salt of greater or less thickness upon their beds. If the pools are deep, which, however, seldom appears to be the case, the deeper strata of the saline solution will be richer in salt than those towards the surface. Although, therefore, water obtained from the surface might not, upon analysis, be found to be as yet near the point of saturation, that at a deeper level might be saturated, and from it salt might be deposited. A powerful evaporation during the warmer months of the year gives rise to descending currents rich in salt, particularly in the middle of the pools, which, in calmer weather, the water of those streams which are poor in saline ingredients does not reach. In this way the quantity of salt in the deeper strata of water is always increasing. In the shallow pools no notable difference in the amount of saline ingredients in the deeper and in the more superficial water can exist; a few hot days will, however, cause them also to become saturated, and thus give rise to a deposition of salt.

We limit our observations to those brines which have been analysed.

The Elton lake, whose greatest diameter is 20, and its smallest

\* G. Rose's *Reise nach dem Ural*. Vol. 2, p. 225.

† *Ibid.*, p. 206.

‡ *Ibid.*, p. 224.

§ *Ibid.*, p. 13.

¶ *Ibid.*, p. 220.

16 werst, lies 19 feet below the level of the ocean. It has flat banks, and may be waded through almost everywhere. On its margins and upon its bed there is almost everywhere crystalline salt. This forms layers from 1 to 2 inches in thickness, which are separated from one another by layers of mud and earth. The streams which empty into it are eight in number. They all contain more or less salt, and consequently carry supplies of this substance into the lake. The most considerable among them is the Charisacha, which is also the only one which continues to flow during the whole year. In the loamy soil which surrounds the lake, numerous small crystals of gypsum are imbedded. G. Rose\* frequently saw crystals of sulphate of magnesia, either single or in little groups, floating upon the surface of the waters.

The composition of the water of the lake is, according to—

		Göbel.†	Erdmann.‡	H. Rose.§
		April.	August.	October.
Chloride of sodium	....	13·124	7·451	3·83
„ of magnesium	....	10·542	16·280	19·75
„ of potassium	....	0·222	....	0·23
Bromide of magnesium	....	0·007	....	....
Sulphate of magnesia	....	1·665	2·185	5·32
„ of lime	....	....	0·036	....
Carbonate of magnesia	....	....	0·038	....
Organic substances	....	traces	0·508	traces
Water	....	74·440	73·505	70·87
		100·003	100·003	100·00

H. Rose remarks, quite correctly, that the water of the Elton lake is merely a concentrated mother-liquor from which, for a long period, common salt has been deposited, and still continues to be deposited during the summer months, the water brought into the lake being at this season less than that which is removed by evaporation. In general, a deposit of common salt takes place in this lake every summer. From 1747 to 1851 there was only one year, 1776, in which such deposition did not take place. The summer of

\* Ibid. Vol. 2, p. 259.

† Reise in den Steppen des südlichen Russland's. Vol. 2, p. 1.

‡ Beiträge zur Kenntniss des Innern von Russland. Vol. 2, p. 252. Erdmann ranked sulphate of soda also among its constituents; since, however, this salt cannot, in presence of chloride of magnesium, exist at temperatures above the freezing point, but is decomposed, sulphate of magnesia and chloride of sodium being formed, the analysis has been corrected accordingly.

§ Poggendorff's Ann. Vol. 25, p. 169.

that year was, however, very rainy and cold. At the distance of two werst from the margin of the lake a well was dug. The uppermost strata of salt were  $\frac{2}{3}$  to  $2\frac{1}{2}$  inches thick. After 46 such strata had been penetrated, their thickness increased to about 8 or 9 inches, and at length, after penetrating 100 strata, a very compact bed of salt was reached.\* There can hardly be a doubt that all these strata of salt are deposits from the lake, and have, for the most part, taken place at periods previous to that at which the salt began to be collected for commercial purposes.

When the temperature of the water of the Elton lake is but slightly diminished, sulphate of magnesia is deposited. Although the portion of water examined by Rose was obtained at a time when the temperature was by no means very high, sulphate of magnesia was deposited upon the bottom of the bottle in such quantity as to be redissolved with difficulty when the temperature was raised. In summer, therefore, only crystals of gypsum and of common salt occur on the banks of the Elton lake; in winter, on the other hand, there is also much sulphate of magnesia, which in summer is re-dissolved by the mother-liquor. According to Pallas, sulphate of magnesia is sometimes deposited along with the common salt in the cool nights during summer, being again dissolved during the day.

Göbel also examined the water of the Charisacha, I, as well as that of the Gorkoi Jerik, II, which likewise enters the Elton lake. In I A and II A, the proportions in which the different constituents occur in 100 parts of the solid contents have been given.

	I.	I A.	II.	II A.
Chloride of sodium ....	4.065	5.25 $\frac{0}{8}$	1.683	2.1 $\frac{0}{8}$
" of magnesium....	0.520	81.43	0.165	81.90
" of calcium ....	....	10.42	0.207	8.03
Sulphate of lime ....	0.124	....	....	10.07
" of magnesia ....	0.283	2.48	....	....
Water ....	95.008	5.67	97.945	....
	100.630	100.00	100.00	100.00

The water of both these rivers resembles those brines which are rich in chloride of magnesium. They must traverse a country, the soil of which is as highly impregnated with salt as that in the

\* Kobülin in Saratow in der Allgemeinen Zeitung. 19 Novemb. 1852.

salt-formations from which such brines proceed. The large quantity of magnesian salts in I, and the abnormally great proportion of chloride of calcium in II, show that pure rock-salt cannot possibly be the source from which these rivers extract their chloride of sodium. The composition given in the analysis I A, approaches so closely the average composition of the water of the sea that the salt-masses which furnish it might be regarded as the residue of evaporated sea-water: for when such a residue is percolated by water, the easily soluble salts are taken up in greater proportion than those which are dissolved with difficulty. Consequently, we observe in I A, that the proportions of chlorides of sodium and magnesium, and sulphate of magnesia, are greater, while that of the sulphate of lime is less than in sea-water. The circumstance that the Elton lake lies below the level of the ocean, is very much in favour of the view that the sea-water which had once covered the depressed tracts of Asia became dried in by evaporation. Owing to the level of the ground, a sea-water concentrated to a certain degree could not have flowed into the neighbouring seas, and therefore beds of pure rock-salt could not have been formed. It is difficult to explain the origin of the large quantity of chloride of calcium contained in the soil through which the Gorkoi Jerik flows. Since no sulphates are present in the water of this river, we are led to conclude that a decomposition of those which were contained in the residue left by the evaporation of the sea-water to dryness has taken place.

At first sight, the great differences in the three analyses of the water of Elton lake may appear somewhat surprising. The sums of the chloride of sodium and chloride of magnesium are, however, nearly equal in all the three; as the one of these two salts decreases, the other increases, and *vice versâ*. The water analysed by Göbel was obtained in spring, when the influx of water is very great, and the evaporation very slight; whereas, Erdmann's specimen was obtained in summer, Rose's in autumn. In proportion, therefore, as the amount of water removed by evaporation becomes greater, the chloride of sodium diminishes—a deposition of it taking place,—while the chloride of magnesium increases. It was to be expected that such an effect might be imitated by experiments. With this view the following were made.

In a solution of chloride of magnesium, common salt was dissolved, and the mixture allowed to stand several days in an open vessel exposed to the heat of summer, until a portion of the com-



mon salt had crystallized. The solution poured off from the crystals consisted of—

Chloride of sodium	....	....	....	8.70
„ of magnesium	....	....	....	16.63
Water	....	....	....	74.67
				<hr/>
				100.00

This agrees pretty closely with what was observed by Erdmann in the Elton lake in August, consequently at a time when common salt had already been deposited. When to the above solution there is added a saturated solution of common salt containing 12.00 of the salt in 33.22 parts of water, a solution is obtained, containing—

Chloride of sodium	....	....	....	14.25
„ of magnesium	....	....	....	11.45
Water	....	....	....	74.30
				<hr/>
				100.00

This also agrees pretty closely with what was observed by Göbel in the Elton lake, in April, consequently at a time when the increased influx of water and the diminished evaporation had given rise to a diminution in the proportion of chloride of magnesium. A portion of the common salt deposited in former years had been again dissolved. It is clear, however, that only a part thereof can have been dissolved; for additional supplies of common salt being constantly carried in by the rivers, and these being also deposited, the deposit of salt must be always increasing. The common salt in the mixture having been found, upon calculation, to amount to 1.12% more than was found by Göbel, it may be conjectured that the water of the Elton lake in April had not yet become saturated with common salt. Probably, however, the difference depends upon the presence of other salts, which diminish the capacity of the water to become saturated with common salt. Slight differences of temperature can exercise only a slight influence on the solvent power of this water. Should the temperature of a saturated solution of chlorides of sodium and magnesium rise from 64° to 77° F., still only 0.01% more of both salts would be dissolved.

To the water of the Elton lake, examined by H. Rose, must be added a solution containing 24.11 parts of common salt and 67.87 of water, in order to obtain a solution which would contain the pro-

portions of chloride of magnesium and chloride of sodium found by Göbel. A solution would thus be obtained consisting of—

Chloride of sodium	....	....	....	14.55
„ of magnesium	....	....	....	10.29
Other salts	....	....	....	2.89
Water	....	....	....	72.27
				<hr/>
				100.00

These proportions approach pretty closely to those actually found by Göbel. Since here, also, the quantity of common salt actually found is less than that calculated, it may likewise be concluded that the water of the Elton lake has in April not yet become saturated with common salt.

In a solution of chloride of magnesium, more concentrated, however, than that employed in the previous researches, common salt was dissolved to saturation, and the solution then exposed to evaporation in the summer heat until some of the chloride of sodium had crystallized. To the saturated solution poured off from the crystals of common salt, sulphate of magnesia was added, and after some time the clear fluid poured off. Its composition was—

Chloride of sodium	....	....	....	5.48
„ of magnesium	....	....	....	22.43
Sulphate of magnesia	..	..	..	0.89
Water	....	....	....	71.20
				<hr/>
				100.00

Hence a solution of chloride of magnesium, saturated with common salt, can dissolve only a very small quantity of sulphate of magnesia. It may be understood then how from such a solution, any sulphate of magnesia dissolved on an increase of its temperature will again be deposited when the temperature falls.

Lastly, when common salt was dissolved in a very concentrated solution of chloride of magnesium, and this exposed to evaporation in the heat of summer for several days until crystals of common salt had been deposited, the composition of the fluid poured off from these was as follows:—

Chloride of sodium	....	....	....	1.18
„ of magnesium	....	....	....	27.35
Water	....	....	....	71.47
				<hr/>
				100.00

The sums of the chlorides of sodium and magnesium in the three saturated solutions mentioned, 24·84, 27·91, 28·53, fall within the limits of the above-mentioned sums of both chlorides in the mother-liquors of salt-works (p. 399), and the two latter come very near the maximum. In the water of the Elton lake also, analyzed at different seasons, the sums of both chlorides, 23·67, 23·73, 23·58, as well as the sums of the chlorides of sodium, magnesium, calcium, and potassium in the Dead Sea, 23·75, 23·60, 26·21 (p. 92), fall within the above limits. The sum of these chlorides, according to Marchand's analysis, 21·41, falls, however, below the minimum of 22·1; the difference, however, being only 0·7.

The proportion of common salt in the Dead Sea, as shown by the analyses I, II, and IV, corresponds very closely with that contained in the water of the Elton lake in August. In like manner the proportion of common salt in the former, according to the analysis III, corresponds pretty closely with that in the water obtained from the latter in April. In the Dead Sea, therefore, there are observed variations similar to those in the Elton lake, though within narrower limits; a circumstance which, when the great volume of water present in the former deep sea is taken into consideration, is remarkable. I cannot help thinking that the water of the Dead Sea employed for the analysis III, which differs so much from the others in regard to the proportions of chloride of sodium and chloride of magnesium, must have been obtained in spring, when a great part of the salt deposited during the previous summer had been again dissolved in consequence of the increased influx of water.\*

A time will come when the Elton lake will have become quite saturated with chloride of magnesium, large masses of this salt being constantly carried into it by rivers. This saturation-point for a temperature of 64° F. is reached, according to my observations, when the chloride of magnesium rises to 24·6%.† From

\* I have not been able to procure the narrative of the United States expedition to the Dead Sea, and could not therefore ascertain whether the season in which the water was obtained is stated; the results of this analysis I have ascertained from Liebige and Kopp's *Jahresbericht*. 1849, p. 613.

† An aqueous solution of chloride of magnesium, of sp. gr. 1·277, continued to absorb water from the atmosphere from the 19th July to the 8th September. Up to the 7th of August it had a temperature of 68° F., it then gradually sunk to 64·5° F. After the condensation had ceased, it presented a sp. gr. of 1·225 at 64·5° F., and contained 24·603 per cent. chloride of magnesium. A solution, therefore, containing this quantity of chloride of magnesium absorbs no more water at a temperature of 60° F. from the atmosphere, nor does it lose any by evaporation. The absorption of the water was very irregular, even during the first ten days, when the temperature of the solution remained fixed. Its minimum was 12 grains,

such a solution no more water can be removed by evaporation; on the other hand, when the summer heat decreases, it absorbs water from the atmosphere. In the Elton lake, however, the evaporation will continue, inasmuch as water is constantly flowing into it. In a warm summer, especially towards the end of summer and in the beginning of harvest, these supplies will be equal to the amount of water removed by evaporation; the saturated solution will remain permanent until, with a decrease of temperature, the evaporation also diminishes. The deposition of common salt will then increase; for a saturated solution of chloride of magnesium can hold only 1%, at the most, of common salt in solution; while the water of the Elton lake, at the time when G. Rose obtained the specimen analysed by his brother, contained in solution 3.83% of common salt. Circumstances will then be still more favourable for the preparation of salt from the water of the Elton lake, which yields about two-thirds of the entire amount of this substance consumed in Russia: it will, however, become less pure, containing more chloride of magnesium.

There now follow the analyses of the water of nine salt lakes, and of a salt-stream in the Kirghis steppes and the Crimea, which as far as IV were made by Göbel.\* Only the more important of them were examined for potassium and bromine. Judging from analogy, it may be assumed that both these bodies will be found in the water of all salt-lakes; since immense quantities of common salt have gradually been deposited by these, bromine will certainly be present in their waters in greater proportion than in sea-water, in brines, or in rock-salt.

	I.	II.	III.
Chloride of sodium .....	17.50	10.54	18.12
„ of magnesium .....	17.95	9.91	5.73
„ of potassium .....	...	...	0.62
„ of calcium .....	1.77	...	...
Sulphate of lime .....	...	...	0.33
„ of magnesia .....	...	8.22	2.30
Water .....	62.78	71.33	72.90
	100.00	100.00	100.00

maximum 32 grains, during the 24 hours. These irregularities depended chiefly upon the variable quantity of moisture in the atmosphere. In the sea-water of warm climates, such as in that of the Dead Sea, the temperature of which in hot summer days may rise to 90° F., a greater amount of chloride of magnesium than 24.6 per cent. might well be attained in consequence of evaporation.

\* Loc. cit. und Poggendorff's Annalen. Ergänzungsband. Vol. 1, p. 181.



	IV.	V.	VI.	VII.
Chloride of sodium ....	21.58	19.000	18.10	22.43
„ of magnesium ....	4.86	5.435	4.20	0.91
„ of potassium ....	...	0.199		
„ of calcium ....	0.89	0.989		
Bromide of magnesium ....	...	0.006		
Sulphate of lime ....	0.07	0.028		0.05
„ of magnesia ....	1.03	...	4.20	0.69
Water ....	71.57	74.343	73.50	75.92
	100.00	100.000	100.00	100.00

	VIII.	IX.	X.	XI.
Chloride of sodium ....	23.928	2.76	14.20	17.80
„ of magnesium ..	1.736	0.07	1.93	0.17
„ of potassium ....	0.101			
„ of calcium ....	...	0.06	0.04	
			* Sulphuret of calcium.	
Bromide of magnesium ....	0.005			
Sulphate of lime ....	0.042	0.27		0.08
„ of magnesia ....	0.346		1.21	0.04
Water ....	73.842	96.84	82.62	81.91
	100.000	100.00	100.00	100.00

I. Red Salt-Lake, two werst from Perekop, almost in the middle of the isthmus which separates the Siwasch from the Black Sea. However much the accuracy of Göbel's analyses is to be relied upon, an error must have been fallen into in the present analysis; for, from what has been already said, it follows that a quantity of chlorides of sodium and magnesium, amounting to 35.45%, cannot be present in any solution. The maximum quantity found in the mother-liquors of brines is 28.8%. But if a brine cannot be brought to a high state of concentration by boiling it, this is much less likely to take place merely in consequence of evaporation.

II. Bitter salt-lake, upon Kigatsch, through which runs the Wolga in its way to the Caspian Sea. In this lake, as well as in 16 others in the neighbourhood of Kigatsch, there is found a deposit 1 foot in thickness of a salt which consists of one equivalent of sulphate of soda, one equivalent of sulphate of magnesia, and four of water. The formation of this salt can only ensue from this, that under certain circumstances, perhaps at a low temperature, a portion of the sulphate of magnesia and chloride of sodium

\* There were also present nitrogenous organic substances.

mutually decompose each other, and thereby produce sulphate of soda, which unites with the undecomposed sulphate of magnesia and chloride of magnesium.\*

III. The salt-lake Tusly, below the great street of Sympheropol, behind Eupatoria.

IV and V. Bogdo lake, north-east of the hill of Bogdo, in the Caspian steppes, has a circumference of 40 werst.† IV is the analysis of Erdmann, V that by Göbel. The chief constituents of both, chloride of sodium and chloride of magnesium, agree so closely with one another that their difference may be owing to the water being taken at different seasons, as in the case of the Elton lake. Sulphate of magnesia cannot be present, since both chemists have detected chloride of calcium.

VI. Salt-lake of Tschakraskoi, not far from the town of Kertsch, and separated only by an isthmus, from 6 to 10 fathoms in breadth, from the Sea of Azoff, with which it is upon a level.

VII. Stephanowa Lake.

VIII. Indersk Salt-lake contains a deposit of salt from  $\frac{1}{2}$  to 3 inches thick, over which stands a saturated mother-liquor 10 inches in depth, from which common salt is constantly separating.

IX. A salt-stream which opens into this lake.

X. The Siwasch, or the putrid sea, upon the east coast of the Crimea, separated from the Sea of Azoff only by a narrow isthmus. It has obtained its name from the very disagreeable odour, which Göbel compares to that of a mixture composed of sulphuretted hydrogen, marsh gas, and of the exhalations which proceed from the mud as it dries upon the banks of salt-lakes. The water of this lake also emits a still stronger odour of sulphuretted hydrogen gas, when hydrochloric acid is added.

XI. Salt-lake at Arsargar, next to the Bogdo lake, the largest in the steppes, between the Ural river and the Wolga.

Among the 14 analyses made by Heine, of the mother-liquors of the brines from different salt-works (p. 399), there are only 3 which show  $\frac{1}{4}$  to  $\frac{1}{2}$  the amount of sulphate of lime which may be dissolved by pure water. The other 11 contain no trace of it,

\* As is known, this double salt may also be formed artificially. It crystallizes, and contains 6 atoms of water of crystallization.

† Erdmann (Archiv. für wissenschaftliche Kunde von Russland. Vol. 9, p. 9) describes a salt lake, north of the hill of Bogdo, having a diameter of from 6 to 9 werst, and only 17·5 inches deep in the middle, which, in continued dry weather, becomes quite dry, depositing its salt in crystals. This lake is probably the Bogdo-See, less probably the salt-lake of Arsargar (IX).

although the brines from which these mother-liquors were obtained, contained this salt. The quantity of chloride of sodium and chloride of magnesium in these mother-liquors falls between  $22.1\%$  and  $28.8\%$ . In one of them, which contains  $0.051\%$  of sulphate of lime, the proportion of chloride of sodium and chloride of magnesium is  $23.8\%$ . Why, then, does this mother-liquor contain sulphate of lime? In both the other mother-liquors, which contain  $0.096\%$  and  $0.053\%$  of sulphate of lime, the amount of the two chlorides is only  $19.1\%$  and  $19.7\%$ ; but besides these they contain chloride of calcium and chloride of potassium, so that in them the quantity of the chlorides taken together rises to  $29.5\%$  and  $29.9\%$ .

From these researches it follows that if the quantity of chloride of sodium and chloride of magnesium in a mother-liquor rises to  $22.1\%$  or  $23.8\%$ , no sulphate of lime can be present; but if, besides these chlorides, chloride of calcium and chloride of potassium are also present, the latter two chlorides do not diminish, but perhaps rather promote the solubility of the sulphate of lime.

In the salt lakes before mentioned the quantity of the chlorides of magnesium and potassium rises in Nos. V, VII, and VIII, to  $24.4$ ,  $22.4$ ,  $25.7\%$ , and yet they contain, certainly, but a small proportion of sulphate of lime. It must, therefore, be left undecided whether the sulphate of lime in a mother-liquor obtained by evaporation of brine at the ordinary temperature is deposited only when the chlorides of sodium and magnesium are highly concentrated, or whether perhaps carbonate of lime was in the analysis, erroneously taken for sulphate of lime; an error which, when the amount of lime found is small, is very apt to be made.

The decrease or complete disappearance of the sulphate of lime in presence of chloride of sodium and chloride of magnesium is also shown by the analysis of the water of the Elton lake, into which, nevertheless, this salt is constantly conveyed by the Chlarisacha. That sulphate of lime is deposited from the Elton lake along with the chloride of sodium, the analyses of the common salt obtained from it show (p. 360). It was also found by H. Rose in several specimens of common salt from the Elton lake;\* Göbel likewise found it in the mud of the same, and it has been already stated that crystals of gypsum occur in the loamy soil which surrounds it (p. 404). The sulphate of lime which is brought in saturated solution by the salt-brook IX into the salt-lake VIII, must in like manner, for the most part, be precipitated, since in the latter it amounts to scarcely  $\frac{1}{8}$  so much as in the former. From the

\* Reise nach dem Ural. Vol. 2, pp. 264 and 268.

salt lake at the Kigatsch which is quite free from sulphate of lime, this salt must also be precipitated : for Göbel found mingled with the double salt of soda and magnesia already mentioned, particles of sand and gypsum.

In the Dead Sea, in like manner, there are found only small quantities of sulphate of lime. Since, however, it is constantly present therein, and that too in double the amount in which it occurs in the water of the Elton lake ; according to Erdmann's analysis, this can only depend on the large quantities of chloride of calcium and chloride of potassium which are contained in the former.

The Great Salt Lake, situated in longitude between  $112^{\circ}$  and  $113^{\circ}$  west from Greenwich, and in latitude between  $40^{\circ}$  and  $41^{\circ}44'$  is a large reservoir, having many streams and one considerable river 500 miles long falling into it. It is one of the many lakes between the Rocky Mountains and the Sierra Nevada of California, and a large one. It has, like these, no outlet to the sea nor any connexion with the Colombia or with the Colorado of the Gulf of California. From not understanding the force and power of evaporation which so soon establishes an equilibrium between the loss and supply of waters, the fable of whirlpools and subterraneous outlets has gained belief, as the only imaginable way of carrying off the waters which have no visible discharge.\*

The principal tributary of the Great Salt Lake is the Bear River.† Whether this be saliferous, though only in a slight degree, has not been determined. The water of a second stream entering the lake does not present the slightest trace of salt. As Fremont did not, while making his investigation, visit other rivers falling into the Great Salt Lake, all information is wanting as to whether any of the stream contain salt. He was, however, informed by Mr. Walker that on the upper part of a river entering the Utah Lake, which communicates with the great Lake, there are immense beds of rock-salt of very great thickness. Further to the southward the rivers which flow towards the Colorado, are, near their mouths, impregnated with salt from the cliffs between which they pass. These beds occur in the same ridge in which, about 120 miles to the northward, and subsequently in their more immediate neighbourhood were discovered the fossils belonging to the oolitic period, and they are probably connected with that formation, and are the deposits from which the Great Salt Lake obtains its salt.‡

\* Report of the Exploring Expedition to the Rocky Mountains, &c., by Brevet-Captain J. C. Fremont. Washington. 1845, p. 275.

† Ibid., p. 132.

‡ Ibid., p. 158.



But it is not possible that this lake obtains its salt from those immense beds of rock salt; for the Utah Lake, subsequently visited by Fremont, contains fresh water.\* Supposing a current to exist between the two lakes, only fresh water can in this way come from the Utah Lake into the Great Salt Lake, but salt water cannot pass from the latter to the former.

It is, therefore, quite uncertain whether any considerable amount of salt be conveyed into the Great Salt Lake by rivers or not. It is, however, quite conceivable that the large amount of salt in that lake may be brought into it by rivers, although the salt is present in these in so small a quantity as not to render their waters in any degree brackish. Numerous rivers have been constantly flowing into the lake ever since the land in this region assumed its present configuration. Immense quantities of water received by it since that time have been removed by evaporation; of necessity, therefore, its saline contents must have increased greatly. This, however, does not exclude the possibility that a salt layer may have been present upon its bed, which has been dissolved by the water flowing into it. According to Fremont, the Great Salt Lake is completely saturated with common salt. The cliffs and masses of rock along the shore of an island in this lake were whitened by an incrustation of salt, where the waves dashed up against them, and the evaporating water which had been left in holes and hollows on the surface of the rocks was covered with a crust of salt about  $\frac{1}{8}$  of an inch in thickness. When exposed so as to be more perfectly dried in the sun, this becomes very white and fine, having the usual flavour of very excellent common salt without any foreign taste; but only a little of it was collected for present use, as there was in it a number of small black insects. Five gallons of the water evaporated roughly over the fire yielded 14 pints of very fine-grained and very white salt. In 100 parts of this salt are contained—

Chloride of sodium	....	....	97.99
„ of magnesium	....	....	0.24
„ of calcium	....	....	0.43
Sulphate of lime	....	....	1.34
			<hr/>
			100.00†

These proportions are very nearly the same as those in which

\* Report of the Exploring Expedition to the Rocky Mountains, &c. By Brevet-Captain J. C. Fremont. Washington, 1845, p. 273.

† The sulphate of soda mentioned in the analysis was reduced to sulphate of lime and chloride of sodium.

the salts are present in sea-water ; it contains, therefore, so little other than common salt, that if it were once concentrated until a deposition of this took place, as pure a rock salt would be formed as the purest of those, the analyses of which have been already given.

From what has been stated, it cannot indeed be determined whether the water of the lake be fully saturated with salt or not, but that it is a highly concentrated solution there can be no doubt. If it be fully saturated, the deposition of salt would soon take place. Up to the present time, however, this has not ensued ; for Fremont remarks that at the distance of half a mile from the island above mentioned the water was 16 feet deep with a clay bottom.

The Great Salt Lake may be compared to the Dead Sea, the only difference between them, being that the former is an almost pure solution of common salt from which none of this substance has as yet been deposited, while the latter, containing the deliquescent chlorides in predominating quantity, must on this account be regarded as a mother-liquor from which much common salt has been already deposited. When, therefore, common salt has after a shorter or longer period been deposited from the Great Salt Lake, its composition will be changed and will come to resemble that of the Dead Sea. From this it may be conjectured that the latter has existed from a much earlier period than the former.

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## CHAPTER XIX.

### SULPHATES.

SULPHATES are not of so general occurrence in springs as chlorides, but next to these they are the most prevalent of the soluble salts which occur in fresh water. In many groups of mineral waters, as in the Bohemian mineral springs at Carlsbad, Franzensbad, and Marienbad, they are very abundant. In these, sulphate of soda is the most predominant constituent, forming, in the Kreuzbrunnen, more than one-half of the entire fixed ingredients, and amounting to three times as much as the common salt, in the others to double the amount of this salt, and

to five times that of the carbonate of soda. In still greater quantity do the sulphates (sulphate of soda and sulphate of magnesia) occur in the so-called bitter waters of Saldschütz, Sedlitz, and Püllna, in which at an average they make up five-sixths of the entire fixed ingredients. These salts must in like manner, therefore, be the most abundant of the soluble salts contained in the rocks from which such springs extract their saline constituents.

There are groups of mineral waters, on the other hand, in which the sulphates, as well as the common salt, diminish and appear in much smaller proportions than the carbonate of soda. This is the case with the groups of mineral springs in the district of the Lake of Laach; it is likewise observed in the numerous mineral springs in the district of the Taurus mountains. Among the former springs, the sulphate of soda reaches its maximum in the mineral water of Roisdorf, near Bonn, in which it amounts to one-seventh, and in the thermal spring of Bertrich, where it forms more than half of the entire fixed constituents.

If we institute a comparison between the Bohemian and Rhine mineral waters above-mentioned, the difference seems to be, that in the former the process of extraction (for we must regard the sulphates of soda, as well as the chlorides, as pre-existing in the rocks) prevails, in the latter the process of decomposition, whereby carbonates of the alkalies are formed.

I examined 38 different fresh-water springs which proceed from felspathic porphyry, granite, syenite, trachyte, dolerite, and basalt.\* The majority contained no sulphate whatever, while only a few seemed to contain sulphate of lime.

In three phonolites, three basalts in the felspathic porphyry of Teplitz, in the gneiss of Bilin, and in the granite of Carlsbad, Struve† found sulphate of potash, and in a few of these rocks also sulphate of soda.

In the phonolite of the Hohenkrähen, in the Högan, C. Gmelin‡ found 0·12% of sulphuric acid, which, no doubt, was combined with potash or soda. In the trachytic porphyry of the Monte Guarda, upon one of the Lipari islands, there is, according to Abich,§ 4·64% of sulphuric acid and sulphur.

There are only a few minerals in which sulphuric acid is found,

\* Germ. ed. Vol. 1, p. 547, &c.

† Über die Nachbildung der Mineralwasser. Heft 2, p. 24.

‡ Poggendorff's Annal. Vol. 14, p. 359.

§ Geologische Beobachtungen, p. 25.

as nepheline. In nosean, hauyne, and azure-stone, it amounts to 12.5%, and is combined with alkalis.

#### A.—*Gypsum*.

None of the sulphates occurs so abundantly as gypsum. It is found in very different sedimentary formations. In the greywacke it rarely appears; Naumann,\* however, mentions several localities where stocks of gypsum make their appearance in this formation.

According to communications from Hunt,† the stocks of gypsum in New York and in Canada rest upon the silurian limestone, and are surrounded by eroded and frequently broken strata of the same rock. This gypsum formation, depending upon an alteration of the carbonate of lime, appears to be still in progress. Hunt's conjecture, however, that the alteration is accomplished by means of springs, containing some free sulphuric acid, is certainly not correct.

The rare occurrence of gypsum in the greywacke limestone, of sulphuretted springs and organic remains in the greywacke formations, and the small amount of sulphates in the springs proceeding from these formations, are relations which stand in intimate connection with one another. The sulphurous springs always occur in the younger sedimentary formations. In the Pyrenees, where they are very abundant, they invariably occur upon the boundary between granite and slate or chalk. If these springs come chiefly from sedimentary rocks impregnated with organic remains, we can distinctly see why the exhalations of sulphuretted hydrogen, which take place at the present day, are connected with carboniferous substances. It may, therefore, be concluded from analogy, that the exhalations of former times, and the formation of gypsum dependent thereupon, were also connected with such substances.

The gypsum in zechstein is generally accompanied by dolomite. The beds of gypsum in parts where it is widely distributed are extremely irregular; it does not present any stratification, and frequently disappears from a series of layers where its existence is accurately ascertained, and this in a more abrupt manner than is ever observed in those strata which occur with it.

On the southern border of the Harz, the gypsum and dolomite are found so intimately associated, and their mutual boundary line

\* Jahrbuch der Geognosie. Vol. 2, p. 306.

† American Journal of Science, 2nd series. Vol. 6, p. 176.



so irregular, that they cannot be separated from one another as distinct layers.

Gypsum is very constantly found between the new red sandstone and the muschelkalk, commonly associated with red and variegated clays which are traversed reticularly by numerous veins of fibrous gypsum. In the muschelkalk of Suabia it is very widely distributed. In the lower section of the red or variegated sandstone of that place, it occurs along with beds of dolomite, and with variegated clay, in the same way as that lying between the variegated sandstone and the muschelkalk. From this group it extends through all the younger sedimentary formations into the tertiary rocks.

Gypsum is one of those bodies which readily changes its locality; it is removed by percolating water, and again deposited in a different place. Accordingly we find it in salt-mines and in brine-pits, as in those of the Dürrenberg near Halein, in those of Hall in the Tyrol, and especially in the so-called kalkschlotten at Mansfeld.

If gypsum is impregnated with organic substances (bitumen), and comes into contact with water, it will, as we have seen (p. 15), be gradually decomposed into sulphuret of calcium, while carbonic acid will at the same time be formed. Should the carbonic acid pass from deeper to higher strata which are likewise undergoing decomposition, it gives rise, in presence of water, to a disengagement of sulphuretted hydrogen, while the gypsum is converted into carbonate of lime. If these exhalations of sulphuretted hydrogen become converted, by attraction of atmospheric oxygen, into sulphuric acid, and this comes into contact with the younger strata of limestone, gypsum will be again formed.

Under such circumstances older beds of gypsum may disappear, being converted into carbonate of lime, while, on the other hand, younger beds of limestone may be converted into gypsum. That such an alteration does actually take place is shown by the occurrence of pseudomorphs of gypsum in the form of calcspar. Of the pseudomorphs, described by Blum,\* from the Zechstein near Eisleben, only one exhibited, and that very indistinctly, effervescence when treated with acids. The alteration had, therefore, been almost completed.

The conversion of gypsum, which is exposed to the influence of the atmosphere, into carbonate of lime, is a very common

\* Nachtrag zu den Pseudomorphosen, p. 23.

phenomenon. G. Schühler\* found that when gypsum had been exposed to the action of the rain, snow, and heat of summer for six months, 13% of carbonate of lime was formed. In the upper parts of the gypsum of Aix, Coquard† found 8·25% of carbonate of lime. In those parts where gypsum is exposed to the atmosphere, it generally effervesces with acids. The carbonate of lime in the gypsum quarries of Montmartre, according to Alex. Brongniart,‡ gradually disappears towards the deeper parts. Lastly, Blum§ describes pseudomorphs of calcspar in the form of gypsum and of anhydrite. Such alterations of sulphate into carbonate of lime are explained by the presence of organic substances in the meteoric waters, and by the influence of the atmosphere upon the sulphuret of calcium formed through their agency. The carbonate of ammonia contained in the atmosphere may also accomplish such alterations.

Althaus|| called attention to an alteration of fibrous gypsum, mingled with clay, into fibrous dolomite, which he observed in the quarries of gypsum near Badenweiler. Lettenmayer¶ analysed the different products of decomposition which occur there.

				I.	II.	III.
Sulphate of lime	....	....		78·33	7·71	0·49
Carbonate of lime	....	....		9·51	50·61	56·69
Carbonate of magnesia	....	....		3·21	37·41	39·04
Carbonate of iron	....	....		....	3·55	3·31
Silica	....	....		6·65	....	....
				97·70	99·28	99·53

		IV.	V.	VI.
Sulphate of lime	....	54·85	....	....
Carbonate of lime	....	....	....	29·09
Alumina	....	4·08	19·77	....
Peroxide of iron	....	2·83	protoxide 6·36	peroxide 2·77
Lime	....	2·32	....	....
Magnesia	....	7·64	22·82	trace
Silica	....	23·70	49·28	68·17
		95·42	98·23	100·03

\* Schweigger's Journ. Vol. 21, p. 213.

† Bulletin de la Soc. Géol., 1841. Vol. 12, p. 347.

‡ Ibid., p. 352.

§ Pseudomorphosen, p. 69, und Zweiter Nachtrag, p. 18.

|| Alberti, Halurgische Geologie. Vol. 2, p. 147.

¶ Ibid., p. 149.

- I. Imperfectly decomposed rock beneath the fibrous dolomite.
- II. Transition from fibrous gypsum to fibrous dolomite.
- III. Perfectly decomposed fibrous gypsum.
- IV. Undecomposed clay in which the fibrous gypsum is imbedded.
- V. Clay occurring in a decomposed state along with fibrous dolomite.
- VI. A crystalline, somewhat porous, rock which accompanies the fibrous dolomite.

I, II, III, show the transition from the fibrous gypsum to the fibrous dolomite, III. The comparison of I, II, and III with IV and V, shows that the source of the magnesia in the fibrous dolomite is the decomposed clay. The alteration of the sulphate of lime into carbonate of lime is probably brought about by the bitumen contained in the clay. During this alteration the silicate of magnesia in the clay is decomposed by carbonic acid, and carbonate of magnesia formed. The carbonic acid proceeds from the decomposition of the sulphate of lime by means of carbonaceous substances; for during this process there is twice the quantity of carbonic acid formed which is required for the alteration of the sulphate into the carbonate of lime. Since the one-half of this carbonic acid acts, while in the nascent state, upon the silicate of magnesia, we are able to account for the otherwise difficult decomposition of this silicate by carbonic acid. This is also favoured by the great tendency of the carbonate of lime to unite with carbonate of magnesia to form dolomite.\* The silicic acid which is separated during the decomposition of the silicate of magnesia, occurs in VI. The carbonate of lime mentioned in this analysis can only proceed from that which has not united with the carbonate of magnesia to form fibrous dolomite.

In the gypsum quarries of Au, near Freiburg, fibrous gypsum occurs in connection with fibrous dolomite under the same relations as near Badenweiler.†

In reference to the above-mentioned association of gypsum with dolomite, the conversion of the former into the latter, when a clay containing magnesia is present, is an interesting phenomenon. At the same time, however, it is not to be maintained that all the dolomite which is associated with gypsum has arisen from the latter.

\* It is well known that magnesia generally has a great tendency to form double salts.

† Loc. cit., p. 152.

As an immediate deposit from water, gypsum is found occurring in dykes and veins. If there should still be a doubt that such is its mode of formation, the presence of gypsum upon mine timber, upon old clothes, and in the so-called "old man," ought to remove such doubt. That gypsum is formed in veins in which sulphuric acid is produced by the oxidation of copper and iron pyrites, &c., when rocks containing lime are present, is self-evident. The occurrence of gypsum in drusic cavities, like every occurrence of this kind, points out decisively that in such cavities it must have been deposited from water which penetrated into them.

Of the pseudomorphs of gypsum in the form of rock-salt we have already spoken (p. 364). Quartz occurs in the forms of gypsum and of anhydrite;\* brown iron-ore in the form of gypsum,† and of bitter spar; and peroxide of iron, in that of anhydrite.‡ The more easily soluble sulphate of lime has been displaced by silica and carbonate of iron, neither of which are easily soluble.

Gypsum is not free from organic remains. The grey or blackish appearance which it sometimes presents, depends on its containing bitumen. In a gypsum-bed in Asia Minor, Ehrenberg§ found infusoria in great abundance. They are large polygastrica with siliceous shells, and are not met with in sea-water. This gypsum is, therefore, to be regarded as a fresh-water formation.

Gypsum occurs as a lapidifying mineral. Alberti and Blum describe such petrifications obtained from the under keuper-formations of Würtemberg. Bones occurring in gypsum are more or less impregnated with sulphate of lime. Bronn describes a coniferous stem weighing above 400 pounds, which is fossilised by this salt.||

When the gypsum has been examined at somewhat greater depths, it is found to be no longer hydrated, but occurs in the anhydrous state as anhydrite. This leads to the conjecture that

\* These very interesting pseudomorphs were found in great numbers at Geyer, in Saxony, by Dr. Krantz, who had the kindness to show me them. They have been fully described by Blum. (Zweiter Nachtrag zu den Pseudomorphosen, p. 93.)

† Of these pseudomorphs in which not a trace of sulphate of lime is to be found, an account has been given by Haidinger. (Poggendorff's Annal. Vol. 88, p. 82.)

‡ Breithaupt describes a pseudomorph of peroxide of iron in the form of anhydrite, which occurs near Eibenstock, in Saxony. At Schunberg, in Saxony, such pseudomorphs are found, consisting of a mixture of quartz and peroxide of iron.

§ Monats Berichte der Berliner Academie, 1849, p. 193.

|| Blum, Nachtrag zu den Pseudomorphosen, p. 178.



gypsum is in great part formed from anhydrite by contact with the atmosphere. It is not surprising that this action should extend to a great depth in some places where the masses of rock are much fissured and torn asunder, thereby allowing a free ingress to the atmospheric air.\*

Blum† mentions several places where a conversion of anhydrite into gypsum has taken place, and among others the valley of Canaria in Switzerland. In this locality the anhydrite, where it comes to the surface, is converted over a wide extent into gypsum. At Bex, according to the observations of V. Charpentier,‡ all the gypsum which occurs upon the surface has arisen by conversion of anhydrite. There are pieces, indeed, in which the transition can be traced. The pure anhydrite is found always in the inner parts of the rock, or in steep parts where, by means of landslips, the interior of the rock has been exposed. Similar appearances have been observed by Alberti§ in the muschelkalk of the south-west of Germany.

Anhydrite takes up, during its conversion into gypsum, about one-fourth its weight of water; if its specific gravity were not thereby altered, its volume would only undergo an increase proportional to the amount of water taken up. But since the specific gravity of gypsum is only four-fifths of that of anhydrite, the volume must, on this account also, increase during the conversion. The expansion of anhydrite during its transformation into gypsum must, therefore, be very considerable. Its effects are very well seen in old galleries of mines which have been formed in anhydrite; in these there occur parts of the walls so loosened that the miners can scarcely pass.

The grey colours of anhydrite, like those of gypsum, depend upon its containing bitumen. Stromeyer|| found in the fibrous anhydrite of Itfeld, in addition to hydrated sulphate of lime, 0.04% of bitumen and 0.087 of carbonic acid. This could not have possibly been retained by an anhydrite which had been exposed to heat, since gypsum is very easily decomposed when heated along with carbonaceous substances. Anhydrite is also found very frequently in metalliferous veins.

Crystalline anhydrite has not yet been formed artificially. The

\* De la Beche, *Geognosie von v. Decken*, p. 578.

† *Die Pseudomorphosen des Mineralreichs*, 1843, p. 24.

‡ V. Leonhard's *Taschenbuch für Mineralogie*, 1821. Vol. 15, p. 336.

§ *Beitrag zu einer Monographie des bunten Sandsteins und Keupers*, 1824, pp. 62 and 69.

|| *Schweigger's Journ.* Vol. 14, p. 375.

circumstances under which sulphate of lime crystallizes in the anhydrous form are not known. Haidinger,\* however, states that the remains of the strongly compressed spaces which, at a former period, contained rock-salt, and which occur at Hall in the Tyrol, are now filled with granular anhydrite. Here then there seems to have been a displacement of rock-salt by anhydrite, and as such displacements can only be conceived to take place in the aqueous way, the occurrence just mentioned affords another argument in favour of the view that anhydrite has been deposited from aqueous solutions. To conclude that anhydrite, because it contains no water, must on this account have been formed in the igneous way, is quite the same thing as if one were to conclude that crystallized anhydrous sulphate of soda is a formation in this way, were it not known that it crystallizes in the anhydrous condition between  $91^{\circ}$  and  $97^{\circ}$  F.

The occurrence of anhydrite along with rock-salt, in formations whose sedimentary origin has never been called in question, would lead to the opinion that the former was introduced subsequently; its formation in the aqueous way being held as an impossibility.

It is not merely the absence of water of crystallization in anhydrite which has led geologists to regard it as a plutonic formation, but still more the disturbances which are exhibited in the strata, and the dislocation of entire rocks surrounding gypsum.† Fr. Hoffmann believed that the gypsum formations occurring in the sedimentary rocks of Northern Germany must be regarded as directly of eruptive origin.‡

Gypsum is a much less fusible substance than lava;§ in order, therefore, to explain its formation in accordance with the Plutonic theory, the interior of the earth must be assumed to present a much higher temperature than that presented by melted lava,—an assumption which is not supported by experience, and has but little probability.

The Plutonic hypothesis places anhydrous gypsum and the crystalline rocks in the same category. It reckons both among the number of the eruptive rocks. Were this correct, it would be strange why, in the subterranean spaces in which the melted masses are supposed to have existed, so distinct a separation of

\* Holgers, *Zeitschrift für Physik*, &c. Vol. 4, p. 225, et seq.

† *Grundzüge der Geologie und Geognosie* von Leonhard, 3rd ed. p. 275.

‡ Poggendorff's *Annal.* Vol. 3, p. 34.

§ It fuses only at the heat of the porcelain veins, and then crystallises as anhydrite. Mitscherlich in Poggendorff's *Annal.* Vol. 11, p. 331.

the anhydrous gypsum from the crystalline rocks should have taken place; for sulphate of lime has never yet been found as a constituent of granite or of any crystalline rock. Just as little does it occur in lava which is decidedly of eruptive origin. Were it an eruptive formation, the spot from which it had arisen must have been under all the sedimentary rocks, consequently beneath the grauwacke group also; but in that case it would be impossible to understand why so little gypsum is now found in these formations.

Within the last few years the hypothesis of the eruptive origin of gypsum has been again advanced with great boldness. A bore-hole at Schöningen, in the Duchy of Brunswick, in which rock-salt was reached at a depth of 1710 and of 1819 feet, passes through the keuper, muschelkalk and upper strata of the new red sandstone. In eight of the strata of these formations, gypsum and anhydrite were found in frequently repeated alternation with marl, claystone, and other rocks. A. V. Strombeck,\* by whom this was pointed out, describes in addition, several masses of gypsum as occurring in that quarter, partly in the new red sandstone, partly in the limits between it and the muschelkalk, and partly, as it appears, in the keuper and oolitic formations. The gypsum masses in question, however, never, according to him, form beds, but merely stocks.

Whatever has risen from the depths of the earth, must stand in connection with these. The gypsum in the bore-hole of the place just mentioned, shows no such connection; there is, therefore, no ground for the assumption that the gypsum stocks in that quarter reach to impenetrable depths. Strombeck would, nevertheless, hold that the gypsum, as seen in the bore, has risen from the deeper parts by sublimation, and has entered, in the form of vapour, between the lines of stratification. The dykes of gypsum, of which a great number occur there, speak decisively, according to him, in favour of an eruptive origin.† Nothing, however, can be clearer than that the springs where the gypsum occurs contain this sulphate, and that such a solution running down through a fissure will deposit gypsum upon its walls. As regards the

\* Karsten und von Decken, *Archiv. für Mineralogie, &c.* Vol. 22, p. 215 et seq.

† Strombeck perhaps appeals to the phenomena observed by V. Loacchi on Vesuvius (*Ann. des Mines* [4]. Vol. 17, p. 323). The most important formations of the gaseous exhalations in 1850 were the gypsum, which consisted of groups of crystalline needles, some of them coloured by chloride of iron, and large crusts from 3 to 5 millimeters thick, which were formed upon the sand and

deposition of gypsum in rock-salt formations generally, we would refer to what has been said in Chapter XVIII.

A deposit of gypsum quite similar to what must have taken place in the case of gypsum dykes, is seen upon the graduation-houses. In the same way as the brine here, while trickling down upon the thorn-bushes, deposits the gypsum which it holds in solution, such a deposit will also take place from water trickling down the walls of a fissure. Very beautiful, sparkling, sparry gypsum, the radii of which always diverge from the thorns, like rays, are found upon the graduation-houses of the salt-works at Nauheim, in Hesse. I have calculated that these stalactites of gypsum, the semi-diameter of which measures  $6\frac{1}{2}$  lines, are composed of at least 216,666 individual concentric layers.\* So many times, therefore, has the juxtaposition of small molecules of gypsum been repeated, and there has arisen, not an accumulation of crystals, the axes of which lie in the most different directions, but crystals, the axes of which have retained unchanged the direction assumed by the crystalline molecules first deposited.

My son, Dr. Carl Bischof, found that when a mixture of felspar and sulphate of lime is exposed to a white heat, sulphates of the alkalies and silicate of lime are generated.†

Masses of melted sulphate of lime could only be conceived to have existed in the interior of the earth in plates, the walls of which consisted of a rock which contained no felspar. But what rock could this have been, since there is no crystalline rock which does not contain silicates of the alkalies, either in felspar or in mica? Were it even assumed that the walls of such spaces consisted of quartz, this mineral also would, at the high temperature supposed, have decomposed the sulphate of lime. Were an extravagant imagination to surmount all these difficulties, it would still be impossible to understand how the supposed masses of melted sulphate of lime could have risen through fissures whose walls contained felspar or quartz, without being decomposed. The gypsum masses, however, are found

lapilli of the crater, the latter substances being unaltered. This gypsum, however, contained a large quantity of hydrochloric acid, sulphuric acid, alumina, potash, peroxide of iron, and a small quantity of protoxide of iron,—substances which are not found in the gypsum of rock-salt formations. But where mineral products exhibit so great a difference in composition, we are not justified in concluding that they proceed from similar origins.

\* German ed. Vol. 2, p. 1054.

† Richard Tilghman founded, upon the above decomposition, a method for preparing sulphate of potash. (Repertory of Patent Inventions, 1847, p. 155.)



lying upon sedimentary rocks which, as the *grauwacke*, *felspar*, or *sandstones*, for example, contain *quartz*. The hypothesis of an ascent of masses of melted sulphate of lime may, therefore, be ranked as one of those reveries which have emanated from the *Plutonic school*, and which science must reject.

As a rock, gypsum makes its appearance in such masses in some parts as to influence the conformation of the surface. It forms hills which rise from flat regions and plains to a considerable height, sometimes gently, at other times more or less abruptly.

In such localities this salt, soluble in 460 parts of water, has been fully exposed to the solvent action of the meteoric waters. Supposing three feet to be the average fall of rain yearly, it follows that should the meteoric water falling upon a gypsum rock become saturated, it will remove nearly half a line yearly. On this supposition, a gypsum rock rising to the height of 100 feet, would in 28,800 years be brought to a level with the surrounding surface, merely by the solvent action of water. The quantity removed mechanically by the water being, however, unquestionably greater than that which is carried away in solution, it is evident that such a gypsum rock must disappear in a much shorter time.

The gypsum which occurs in the form of beds, is very much fissured; the meteoric waters, therefore, penetrate into its interior, where they have an opportunity of coming into repeated contact with it, and of becoming saturated. If the neighbouring beds are either not at all or but slightly fissured, the meteoric water which sinks into the surrounding parts may still find its way into the gypsum, so that far more than half a line yearly will be dissolved and carried away. Hence arise the large cavities which occur in the interior of many gypsum rocks, as well as the frequent *land-slips* which take place over such rocks.

Lastly, if the beds of gypsum are covered by other sedimentary rocks, and the meteoric water reaches them, it is clear that after a shorter or longer period they may be completely washed away.

The strata overlying the gypsum, therefore, undergo a gradual subsidence. If from a bed of gypsum more be removed in one part than in another, unequal subsidence takes place. In this way may be explained the disturbances of stratification and dislocations of whole series of rocks.

If the gypsum forms a partial stratum beneath beds of clay or marl, for example, and is gradually removed by water, these beds subside only in that part which was occupied by the gypsum; their stratification is therefore disturbed. In a word, when the founda-

tion is washed away, these subsidences and fractures take place: where the gypsum has not originally been present, or has not been washed away, then all remains undisturbed.\*

The removal of gypsum by water, however, is not the only cause of disturbance in the stratification of overlying formations. We have seen (p. 423) that anhydrite, during its conversion into gypsum, undergoes a very considerable increase in volume; beds, overlying anhydrite which is undergoing such a change, will therefore be upheaved. It may be that the considerable elevation which, according to Emmons, the gypsum in Oneida and Onondaga, in the State of New York, has undergone, owes its origin to this cause. If the conversion of anhydrite into gypsum takes place to a greater extent in one part than in another, the overlying strata will be unequally upheaved or tilted.

We have, then, become acquainted with causes which may give rise to subsidences or elevations of stratified rocks overlying gypsum or anhydrite. In many cases where the conversion of anhydrite into gypsum, and the washing away of these substances, go on simultaneously, these opposing actions counterbalance each other; in such cases little or no disturbance will ensue in the overlying strata.

When the action of water, in giving rise to disturbances of stratification, admits of being so clearly recognised as in the instances above mentioned, it is more than ridiculous to attribute them to plutonic action.

Against the sedimentary origin of gypsum, the objection has been urged that it is destitute of the distinguishing character of sedimentary rocks—stratification. In relation to crystalline masses, however, we cannot speak of an appearance which is peculiar to mechanical deposits. The deposition of substances which are held in solution, follows quite different laws from those which regulate

\* German edition, 1847. Vol. 1, p. 542. Engelmann (Erman's Archives, 1850, Vol. 6, p. 701) mentions partial subsidences of considerable tracts of land in Courland, consequent upon the dissolving and washing away of the underlying limestone and gypsum. Ebelman (Comptes Rendus, Vol. 33, 1851, p. 678) mentions, that in the keuper of the Haute Saone the loam-coal rests upon masses of compact gypsum. The deeper parts of the coal are cemented by gypsum, towards its upper parts, and in the outcrop the gypsum has been removed by water, and a marl has been left which enfolds with numerous bends the gypsum masses which have not come into contact with the water. The marl, however, also rests immediately upon the muschelkalk, the gypsum having here quite disappeared. The lenticular masses of gypsum in the basins of Paris also owe their form, according to Ebelman, to the solvent action of water; for they occur most frequently beneath the summit of a hill where they were least exposed to such action and least frequently upon its declivities.

the deposition of substances held merely in suspension. During crystallization we observe that the crystals are deposited chiefly upon projections, upon sticks or rakes, as is the case with the crystals of green vitriol; or upon threads, like those of candied sugar. If a fluid in which crystallization is going on, a saturated solution of green vitriol, for example, be tested by suspended particles of hydrous peroxide of iron, distinct layers of crystals and of mechanical deposits are not formed; on the other hand, the crystals are deposited upon the sides of the vessel which contains the solution, and upon rakes, while the suspended particles form true strata upon the bottom of the vessel.

In reference to gypsum, therefore, we can as little employ the term stratification as in reference to rock-salt; and still less can we conclude from the absence of stratification, that it is of plutonic origin, or has at least subsequently penetrated between adjacent rocks.\*

#### B.—*Sulphate of Magnesia. Sulphates of the Alkalies.*

Sulphate of magnesia occurs as an efflorescence from the soil in many places; sometimes, particularly after heavy falls of rain, in large quantity. It is met with in this form in the Steppes of Siberia, in Andalusia, Catalonia, upon the island of Milo, and in all mines, quarries, caverns, &c. It is found in the clefts of clay slate and of limestone, upon brown-coal, as also in marly and in metalliferous beds. On the Jura mountain, in the Canton of Aargau, it is found in the form of veins, often  $\frac{1}{2}$ " to 1" in thickness, in hard gypsum, and extending to a depth of more than 50 feet below the earth's surface.† It does not appear to be present in crystalline rocks, the gneiss at Freiburg excepted. Hermann states,‡ that in the marls on the declivity of the Caucasus, which generally contain gypsum, as also silicates of soda and magnesia, a formation of sulphate of soda and sulphate of magnesia takes place. Hence the phenomenon which in summer is observed on the way from Georgiëff to Piatigorsk, of two plains presenting the aspect of being covered with snow. These constitute the beds of two small lakes which have been formed in a bed of marl, similar to those

\* Naumann (Jahrbuch der Geognosie, Vol. 1, p. 681) observes, however, that the granular and compact gypsum occurs at one time distinctly stratified, at another quite unstratified. According to Lösché (Naturhistorisch Zeitung Jahrgang, Vol. 1, p. 260), the masses of argillaceous gypsum in the rock-salt beds at Aussee, in Styria, show, for the most part, distinct stratification.

† P. Bailey, in Annal. der Chemie und Pharmacie. Vol. 25, p. 328.

‡ Poggenдорff's Annal. Vol. 22, p. 348.

above-mentioned. The water which collects in these lakes during winter and spring, dissolves the soluble salts contained in the marl, and being in summer removed by evaporation, leaves behind a crust often many inches in thickness, consisting of sulphate of magnesia and sulphate of soda.

According to Suckow,\* the efflorescence of sulphate of magnesia in the vicinity of Jena, depends upon the decomposition of the carbonate of magnesia contained in bitter spar, by means of gypsum. Mitscherlich† found that a solution of gypsum is fully decomposed, in the course of 14 days, into carbonate of lime and sulphate of magnesia. Struve‡ holds gypsum, carbonate of lime, decomposed phonolite, and decomposed basalt, to be the chief substances from which are derived the materials for the formation of the salts contained in the bitter waters of Saidschütz and Sedlitz in Bohemia. After the water which percolates these minerals has taken up sulphate of lime, this salt and the silicates of soda and magnesia decompose each other, giving rise to sulphate of magnesia, sulphate of soda, and silicate of lime. By exhausting the marl of Saidschütz and Püllna with pure water, Struve actually obtained a saline solution in which these constituents were present in nearly the same proportions as in the bitter water of these places.

When a solution of gypsum is allowed to stand over silicate of magnesia, a slight decomposition is observed after a few hours to have taken place, while lime and magnesia are found dissolved in the fluid; even after an interval of 14 days, however, I found that the decomposition had made little further progress. In nature, a solution of gypsum must certainly remain for a long time in a bed containing silicate of magnesia, in order that the decomposition should perfectly take place.

Sulphate of magnesia being contained in large quantity in several rivers, this salt cannot, so far down as the meteoric waters penetrate, remain limited to particular localities, whether it be present as such, or formed in a way similar to that above mentioned, but must become more widely distributed. Having already shown (p. 363) that a part of the sulphate of magnesia contained in the sea-water must, when the latter was evaporated to dryness, have been left in formations deposited from the sea; that which is found in efflorescences and in the water of rivers may, for the most part, be merely extracted.

\* Journ. für Pract. Chem. Vol. 8, p. 409.

† Jahrbuch der Chemie. 2nd Auflage. Vol. 2, p. 144.

‡ Ueber die Nachbildung der Natürlichen Heilquellen. Vol. 2, p. 55.



Sulphate of potash is more rarely met with than sulphate of soda. In mineral springs it often occurs along with the latter, though in small quantity. It might be found more frequently, were it looked for with greater care. It is found in many of the lavas of Vesuvius, as well as on the mouth of the crater, and sometimes as an efflorescence from the volcanic masses.

Sulphate of soda, besides occurring in springs, is found in the gypsum of the Kneiper, in clefts in decomposing mica-slate at Reidt, near Amstäg in Switzerland, and in argillaceous gypsum, also in beds of rock salt.\* It is also met with as an efflorescence from marl and from the soil in many places, as in the Caspian and Silurian steppes,† in the neighbourhood of certain lakes, and in that of certain morasses in Hungary. It is likewise sometimes seen as an efflorescence upon volcanic products, as upon the lava thrown out by Vesuvius in 1813.

It has been already stated that one source of this salt may be the mutual decomposition of gypsum and silicate of soda. By digesting for eight days in water containing gypsum, a pound of clinkstone which had been previously washed with water, and had therefore lost the greater part of its soluble constituents, Struve obtained nearly an ounce of sulphate of soda.

In the sea the constituents of sulphate of soda are present; on evaporating sea-water at the ordinary temperature, this salt is however never found among the ingredients which are deposited. But if the waters of the sea or of a salt lake overflow their boundaries, and if a mineral water containing carbonate of soda enters from another quarter, sulphate of soda will be formed by the decomposi-

\* At Hall, in the Tyrol (Kopf, in Karsten's, and von Dechen's Archiv für Mineralogie, Vol. 15, p. 442), and in the Dürrenberg, at Hallein (Schwll, in von Mohl's Jahrbücher, &c., p. 212). In the latter place it occurs in and near the rock-salt. It is also often disseminated through this. In the clay it is only found mixed with rock-salt. Sulphate of magnesia occurs not unfrequently along with rock-salt and sulphate of soda.

† According to Darwin (Naturwissenschaftliche Reisen German Translation, by Dieffenbach, Vol. 1, p. 74), there are found in the mud upon the banks of a large salt-lake fifteen miles from the town of El Carmen, upon the Rio Negro, countless large crystals of gypsum and of sulphate of soda. In like manner there occur in many parts of South America, where the climate is moderately dry, incrustations of this salt, along with very small quantities of common salt. Nowhere did he find it so extensively distributed as in the neighbourhood of Bahia Blanca. So long as the soil is damp in these places, nothing is seen but an extended plain of black muddy ground; but when it becomes dry during the hot season, square miles of land are seen covered with sulphate of soda, as with a moderate sprinkling of snow. The places where such efflorescences are found occur in flat districts, raised only a few feet above the level of the sea, and presenting the appearance of having been shortly before overflowed with water, or in the overflowed districts in the vicinity of rivers.

tion of the sulphate of lime and sulphate of magnesia present in the former. In this case, however, it will be mingled with a much greater quantity of common salt than was contained in that found by Darwin. It may also be formed when a mineral water, which contains carbonate of soda, penetrates a soil impregnated with gypsum and sulphate of magnesia.

### C.—*Heavy-Spar.*

Heavy spar has not yet been found as a mineralogically defined constituent of crystalline rocks. In the form of dykes, however, it occurs in most of these rocks, and very frequently in many sedimentary rocks. As such it is found in granite, porphyry, gneiss, mica-slate, hornblende slate, syenite, diorite, amygdaloid, and serpentine, as well as in clay-slate, also in the carboniferous group, in red conglomerate, in zechstein, in saccharoid limestone, and mountain limestone. It also very frequently occurs in the metalliferous veins present in these rocks.

When it alone, or in greatly predominating quantity, fills the fissures in the crystalline rocks, its formation in the wet way might for a moment seem doubtful. Its occurrence in drusic cavities and in clefts in different sedimentary formations, in chalcedony, in ferruginous quartz in cavities, in sphærosiderite, in wood-stone, in alum-stone, and lastly, as a lapidifying mineral, in belemnites, ammonites, and wood,\* speak decisively for its being a deposit from water. The impressions which have been left in its crystals by quartz and calcspar, are in like manner explained by its having been formed in this way.

The aqueous origin of heavy-spar is likewise indicated by its being frequently found associated with minerals, such as brown iron-ore and ochrey iron-ore, calcspar, &c., which can only have been formed by the action of water,—or with others, such as native mercury, arsenic, sulphur, and cinnabar, which at the high temperature of the supposed melted baryta would have been volatilized.† The occurrence of native silver in metalliferous veins in granite, at Wittichen in Baden, in wirelike, arborescent, and beautifully zigzag forms, associated with heavy-spar and other dyke masses, deserves especial notice. The larger and

\* Blum, *Nachtrag zu den Pseudomorphosen*, p. 173.

† Even the supposition that these bodies were volatilized at a later period, and after the baryta had already cooled, and that they filled the crevices left in it, is still opposed by the fact, that the easily fusible and volatile substances would certainly have risen from the interior of the earth earlier than the difficultly fusible and non-volatile sulphate of baryta.

smaller particles of this mineral seem as if partly held together and supported by wires of silver. This metal must, in every instance, have been present earlier than the baryta-spar. Had the latter entered subsequently as a melted mass, these silver threads must have been fused together into a single lump, since baryta-spar is fused with far more difficulty than silver. Should it be assumed that they both entered the fissures at the same time in a melted state, the very difficultly fusible sulphate of baryta would, notwithstanding, have passed into the solid form sooner than the easily fusible silver. Had also the silver filaments originated in a way similar to that in which the small vegetations are formed during the solidifying of perfectly pure silver, it would still remain inexplicable how these fine filaments could have supported the long-since solidified baryta, and have coalesced with it. All these appearances are easily explained, however, on the supposition that drops of water holding sulphate of baryta in solution fell upon the earlier formed silver wires and deposited it upon them.

The only instance yet known in which compact heavy-spar occurs in the form of a bed, is at Meggen upon the Lenne. For our knowledge of it we are indebted to the researches of Dechen.\* It is of no great thickness, but has a superficial extent of about two English miles. Its floor is formed by clay-slate; its roof is, in like manner, formed by the same rock, and upon this again rests limestone. No one will seek to oppose the view taken by Dechen, that the layer of baryta-spar, as well as the limestone, have been deposited from water, whether chemically or mechanically must be left undetermined.

Sulphate of baryta occurs pretty frequently as a cement, as in the so-called arkose upon the granite declivities of the Morvan, where it has cemented the disintegrated and decomposed constituents of the granite.† In the tertiary formations, in the district of Keuznach, there are found numerous globular concretions, measuring from 3 lines to 5 inches in diameter, and consisting partly of sulphate of baryta, partly of sand and clay cemented together by this sulphate of baryta. In one place they are kneaded together into flat cakes; in another place they form a layer ten feet in thickness, the crevices in which are filled with small fragments of porphyry and sand. In the interior of the rounded

\* Archiv, für Mineralogie, &c. Vol. 19, p. 748.

† Kritische Beleuchtung der Werneriten Gangtheorie von v. Beust. 1840, p. 6.

concretions there is found loose sand; frequently also tertiary shells consisting of pure sulphate of baryta, or wood petrified by it.\* Similar concretions are found in the marl of the tertiary rocks at Bologna, also in the alluvial clay at the environs of Leipsic. At Münzenberg, in the Witterau, a sandstone occurs the cement of which in like manner consists of sulphate of baryta.†

How can one then, in the face of such facts as these, still attribute a plutonic origin to sulphate of baryta? The beds and concretions above-mentioned can only have been formed as deposits from an aqueous solution. The aqueous origin of sulphate of baryta is further shown by the tendency to the crystalline form seen upon the surface of many of the concretions found at Kreuznach, as well as by the crystals of sulphate of baryta which occur in the sandstone at Münzenberg.

Calcspar, bitter-spar, iron-spar, carbonate of lead, quartz, chalcedony, peroxide of iron, brown-iron-ore, iron pyrites, white iron pyrites, psilomelan, and steatite, occur in the forms of heavy-spar. These minerals have consequently displaced the sulphate of baryta, which latter could have been removed only by aqueous fluids. The four carbonates above-mentioned are decidedly more soluble in water than sulphate of baryta; the same may also be said of quartz and chalcedony, if it be supposed, as was no doubt the case, that it was in its soluble modification that the silica displaced the sulphate of baryta. This, however, is opposed to the law that the displacing substance is always more difficultly soluble than the substance which is displaced,—a law which has been found to apply in so far as concerns those cases in which the solubility of the two bodies can be ascertained. It may, therefore, be conjectured that in the displacement pseudomorphs after sulphate of baryta this has been removed, not as such, but after being decomposed and converted into soluble compounds by means of the substances held in solution by the water. As regards peroxide of iron, brown-iron-ore, psilomelane, and steatite, it cannot be determined whether they be more easily or more difficultly soluble than sulphate of baryta. Lastly, whether pseudomorphous iron pyrites and white iron pyrites, in the form of heavy-spar, have been formed in the way of displacement or of alteration, cannot be determined. It is at

\* Nöggerath and Dellmann, in den Verhandlungen des naturhistorischen Vereins der Preuss. Rheinlande, 1846, p. 63; and 1847, p. 66.

† According to a communication by my friend Blum.



least conceivable that the sulphate of baryta was altered by organic substances contained in the same water by which the carbonate of iron was dissolved and converted into sulphuret of iron. The rarely occurring pseudomorph\* of carbonate of baryta in the form of sulphate of baryta, appears to have been formed in the way of alteration rather than by displacement. In it also the sulphate of baryta may have been converted by organic substances into sulphate of barium, and this again converted, by carbonic acid or alkaline carbonates, into carbonate of baryta; or the sulphate of baryta may have been converted into carbonate of baryta by moderately warm water containing alkaline carbonates.

It is particularly worthy of notice that baryta-spar itself, on the other hand, has never yet been found in the form of any other mineral. This, however, is only what might have been expected, seeing that it exceeds most other minerals in difficulty of solubility. The Plutonists might employ this as an argument against the aqueous origin of sulphate of baryta, did not the numerous phenomena already mentioned speak quite decisively on this point. The belemnites and ammonites, which are found lapidified by sulphate of baryta, may be regarded as displacement pseudomorphs in the form of these organic bodies.

There can be no doubt that the crystal of baryta-spar which was found by W. Niccol†, and which contained a cavity filled with fluid, was formed in the wet way. When one of the faces of this crystal was rubbed down upon a dry stone until the cavity was opened into, the fluid escaped and formed several drops upon the stone. After twenty-four hours, each drop was found converted into a crystal of sulphate of baryta. Brewster's testimony is a sufficient guarantee for the accuracy of this observation.

Upon an unprejudiced consideration of the various relations under which baryta-spar occurs, one cannot for a moment entertain a doubt that it has been formed in the wet way; its chemical properties are such as equally to lead to the same conclusion. In the furnace of Sefström, in which with coke, and by the employment of hot air, I have reduced to a perfectly fluid state the different crystalline rocks, from basalt to granite, the sulphate of baryta could be brought into this condition only where it was in contact with the crucible; the inner portions of the mass, on the other hand, could hardly be made so fluid as to run together.

\* Breithaupt, die Paragenesis der Mineralien, p. 202.

† Berzelius Jahresbericht, Vol. 7, p. 192.

When large dykes are found filled with heavy-spar, the explanation that this mineral has passed into them in a melted state, might at first sight appear admissable. It becomes more difficult, however, where we see it filling narrow fissures; a dyke, for example, eight inches thick, such as is found in serpentine in the district of Waldheim, in Saxony; for however high we assume the temperature of such a melted mass to be, the low temperature of the walls of the fissure must have very soon brought it to the solid state,—and before, indeed, it had passed up into the fissure to any considerable height. What rock is there, however, which is so difficultly fusible as baryta-spar, and which therefore could have resisted the high temperature of that substance in a melted condition? Should we not, had the sulphate of baryta risen as a melted mass, have found the rocks between which it passed, fused at the points of contact with it into a continuous mass with it.

G. Leonhard\* sought, with singular obstinacy, to defend the view that the sulphate of baryta in the dykes traversing the granite and porphyry near Schriesheim, in the environs of Heidelberg, one of which is from 8 to 10 feet in thickness, has been injected from beneath in the condition of a melted mass. From my own examination of this dyke I find, however, that not one of his arguments can bear a strict criticism.

In the water of a gallery in the vicinity of the dyke mentioned, I have not found a trace of sulphates. As a portion of the water which filters through the fissures and clefts of the granite, collects in this gallery, no sulphates of the alkalies from which sulphate of baryta might be formed, can be present in this rock. These salts have either been already extracted, or they were not originally present, and could not therefore have contributed to the formation of the sulphate of baryta. In two specimens of granite from the neighbourhood of the dyke in question, I found minute yet very perceptible traces of baryta. This, however, could not have been present as sulphate; for when the granite was decomposed with carbonate of potash by strong heat, I could detect in the fluid filtered from the silica no trace of sulphate of potash. The only explanation which is left, therefore, is that the baryta was present as silicate, probably as a constituent of the felspar contained in the granite.

I have in vain tried to detect baryta in the amygdalite mentioned below, from Idar, as well as in several calcspars and in druses in

\* German edition. Vol. I, p. 603.

basaltic rocks in which more or less distinct traces of strontia were found.\*

By the following experiments I endeavoured to ascertain whether it was possible for the sulphate of baryta to exist as such in the crystalline rocks, were they of plutonic origin. To 100 grains of finely pulverised felspathic porphyry, 10 grains of sulphate of baryta, prepared by precipitation, were added, and the mixture exposed for an hour in a platinum crucible to the heat of a powerful blast-furnace. A vitreous mass was obtained, which upon being finely pulverised, and exhausted with warm water, yielded a fluid which did not exhibit the slightest turbidity on addition of chloride of barium. Not a trace, therefore, of sulphate of baryta had been decomposed, and no alkaline sulphate formed. From this experiment, it appears probable that heavy-spar might exist in crystalline rock in a state of igneous fusion, without undergoing any decomposition.

The experiment which follows was made with a view to ascertain the relation in which the sulphate of baryta stands to other salts occurring in the mineral kingdom. Silicate of baryta, a salt

\* The detection of baryta in rocks, when present only in minute traces, is attended with peculiar difficulties. If the alkaline carbonates which are employed to decompose a mineral contain merely a trace of an alkaline sulphate, sulphate of baryta, in so far as this earth is present, will, in the subsequent treatment with hydrochloric acid, be thrown down. The sulphate of baryta thus precipitated may therefore be taken for undecomposed mineral, or for silica. When only a trace of baryta is present, it may entirely escape detection in presence of the alkaline sulphate. Minute quantities of sulphates, which may have been left by the water with which the minerals had come into contact, may likewise give rise to such a fallacy. Hence it is necessary to exhaust every rock with distilled water before commencing the examination for baryta. If carbonate of baryta be employed to decompose the mineral, it cannot, of course, be determined whether baryta really existed in the mineral or not. Even where hydrofluoric acid is employed as the decomposing agent, this likewise may be detrimental, if, as is commonly done, sulphuric acid be added during the evaporation required to volatilise the fluosilicic acid; sulphate of baryta will in that case remain behind, and will be obscured by the sulphate of lime. In the numerous analyses of minerals and rocks which have been undertaken by the ablest chemists, baryta, if present in only minute traces, may have easily escaped detection.

According to Fresenius, the carbonate of baryta and carbonate of strontia in the Krähnchen of Ems amount to 1.931 of the carbonate of lime; supposing the former two carbonates to be present in equal proportions, the carbonate of baryta would only amount to 1.1862 of the carbonate of lime. Should these two earths be present in a felspar such as orthoclas, the chalk in which makes up, at the most, 3 per cent. in the same relative proportions as they are contained in the above mineral, the baryta earth would in such an orthoclas amount to 0.0016 per cent. It is not at all difficult to see that so minute a proportion might easily escape the notice of the chemist if his attention is not particularly directed to baryta, and especially when, as is generally the case, the quantity of mineral employed for the analysis is comparatively small.

which as yet has been but little examined, was prepared by decomposing an aqueous solution of silicate of soda by means of chloride of barium added in excess. The precipitated silicate of baryta was separated by filtration, and washed upon the filter with water until the fluid which passed through the filter no longer exhibited any turbidity on addition of nitrate of silver. The silicate of baryta so prepared dissolves in from 20,000 to 27,590 parts of cold water.\* In water at the temperature of  $212^{\circ}$  it is much more soluble, only 1000 parts of water being required. According to analysis, it consists of 1 equivalent of baryta, 5 of silica, and 3 of water.

A cold solution of this silicate is decomposed by sulphates of the alkalis, by sulphate of lime, and by sulphate of magnesia; sulphate of baryta being precipitated, while a silicate is formed, which in the case of the two alkaline silicates remains in solution, but in the case of the two earthy silicates is precipitated along with the sulphate of baryta.†

The circumstance that the silicate of baryta is decomposed by all soluble sulphates, is due to its being soluble, while the sulphate of baryta formed in such cases is insoluble. It may with good ground be assumed, that the solubility in question is one of the causes why no single silicate of baryta is found in the mineral kingdom; although at the same time such a silicate might be expected to occur, seeing that the other alkaline earths, lime, and magnesia are met with so frequently, both as simple and as compound silicates. This, however, cannot be the only cause, inasmuch as other soluble salts, such as gypsum, for example, are met with in the mineral kingdom. We must rather suppose that the

\* The exceedingly unstable nature of the silicate of baryta is remarkable: it separates from its solution when this is subjected to evaporation; the slightest breath is sufficient to effect this. It is even more unstable than the silicic acid which is deposited when fluosilicic gas comes in contact with water.

† Sulphate of strontia, when added to the solution of silicate of baryta, gave rise to no turbidity. It is not to be supposed, however, that these two salts do not decompose each other; for easily soluble baryta salts, such as the chloride of barium, caused a very perceptible turbidity in a solution of sulphate of strontia. The latter salt requires for its solution 3600 parts of water. Since now silicate of baryta requires 20,000 parts, the amount of the water, when both solutions are brought together, rises to 23,600 parts, in which are dissolved two parts of both salts. In a solution diluted to this extent, however, an appreciable turbidity must still be produced, since when one part of chloride of barium is dissolved in 200,000 parts of water, the solution is still rendered turbid, after some time, by sulphuric acid.

It is very remarkable that a cold solution of silicate of baryta is rendered so turbid by carbonate of potash or of soda that sometimes a white flocculent precipitate is formed, not, however, by carbonate of ammonia. As the carbonate of baryta thus formed ought to dissolve in 4,300 parts of water, while in the present case 20,000 parts are present, it would seem to form in such circumstances a difficultly soluble double salt.



frequent occurrence of sulphates in springs, is that which renders a silicate of baryta impossible. Did this silicate occur in any rock, the percolating water would extract it, and so soon as such solution came into contact with any soluble sulphate, sulphate of baryta would immediately be formed. From this alone, it is obvious that silicate of baryta and any alkaline sulphate could not exist together in a rock, but only sulphate of baryta and silicate of the alkali. It is therefore, a certain indication of the absence of silicate of baryta in a rock, when the springs proceeding from the latter contain sulphates. Only in such rocks as are quite free of these salts can silicate of baryta possibly occur.

Not a trace of sulphates being found in the water from the old gallery before-mentioned, they can just as little be present in the granite from which that water proceeds. Our supposition that the baryta found in this granite is present as a silicate, is therefore well established.

Compound silicates of baryta, harmotome, and brewsterite, the only ones yet known, occur but rarely, and that chiefly in drusic cavities and clefts in crystalline rocks. The question now arises, in what combination the baryta may be present in basaltic and similar crystalline rocks in the drusic cavities of which harmotome is found? It was natural to conjecture that this mineral, which is a double silicate of baryta and alumina, is also present as such in the rocks, but in the anhydrous condition, and that it does not become an hydrated silicate until it is acted on by the water. Analogy is in favour of this conjecture, labradorite being probably the source from which most of the zeolites proceed. There is no difficulty in conceiving that labradorite may, by taking up five equivalents of water, be converted into scolozite and natrolite. If, therefore, a labradorite should be found in which the baryta had entirely or partially taken the place of lime, it might with equal probability be conceived that from such a baryta labradorite, by addition of five equivalents of water, harmotome and a zeolite containing soda might arise.\* Indeed, it would be very interesting to find such a labradorite. It is not beyond the bounds of probability, that among the many labradorites which have been

\* In harmotome there are 3 equivalents of baryta and 4 of alumina; in labradorite 3 of lime and 4 of alumina. The bases are consequently, if baryta has taken the place of lime, present in both minerals in equal proportions. Should, therefore, a barytic labradorite be found, it is only necessary that 18 equivalents of water and 2 of silicic acid should be added in order to obtain harmotome: for the latter contains 10, while the labradorite contains only 8 equivalents of water.

analyzed, one or other of them might have contained, besides lime, traces of baryta also, which escaped the notice of the chemist. This is the more probable from the circumstance that brewsterite contains, besides lime, baryta and strontianite.

By decomposing sulphate of baryta in various ways, the chemist obtains baryta and all its compounds. Some of these processes may be conceived as possible in the mineral kingdom also. The sulphate of baryta cannot be decomposed by silicates, but the silicate of baryta may be decomposed by all soluble sulphates. On this account there is very little probability that the sulphate of baryta is the salt which nature employs for the formation of the silicates, harmotome and brewsterite, as well as psilomelane. These considerations also lead to the very probable conjecture, that in the mineral kingdom there exist silicates of baryta from which are formed, not merely the two hydrated silicates, but also psilomelane.

Since the carbonate of baryta is found to be decomposed at ordinary temperature by sulphates of the alkalies, and by sulphate of magnesia, &c., such may have taken, and may still take place in the mineral kingdom also. Seeing that these sulphates are so abundant in many waters, supposing that such waters should become mingled with others holding carbonate of baryta in solution, sulphate of baryta will be formed, as is distinctly seen when to water which has stood over carbonate of baryta, a solution of a sulphate is added. The formation of the carbonate of baryta by decomposition of a silicate of baryta, through the agency of carbonated waters, is easy to conceive on the supposition that the latter salt exists in rocks; it is the same process as takes place in the conversion of the silicates of the other alkaline earths and of those of the alkalies into carbonates.

Haidinger\* states, that the carbonate of baryta in the mountain limestone of Alston Moor is met with in all stages of conversion into sulphate of baryta. The change commences at the surface, giving rise to the formation of a crust of greater or less thickness, consisting of very small crystals of heavy-spar.† Blum‡ remarks,

\* Poggendorff's *Annal.* Vol. 11, p. 376.

† These alterations are chiefly seen upon those parts of the dykes which lie near the surface. At Anglesark, in Lincolnshire, it has even been observed that in the veins which intersect strata of sandstone, slate, and coal, and which here in particular contain lead glance, baryta-spar, and witherite, the carbonate of baryta occurs in the deeper parts, the sulphate, on the other hand, in the parts at the surface. (W. Phillips's *Mineralogy*, 1823, p. 133.) This receives its explanation from the circumstance that the water by which these alterations have been effected flowed from above downwards.

‡ Loc. cit., p. 45.

that a nucleus of the previously existing substance is still frequently present, or cavities are seen, caused by the removal of the carbonate of baryta without being replaced by sulphate of baryta. He observed very small crystals which were quite hollow, and consisted of two or three crusts separated from one another by fine interstices. Had change in these consisted merely of an alteration of the carbonate into sulphate of baryta without removal of any portion of the former salt, the volume of such crystals must have undergone an increase in the proportion of 1 to 1.143. In this case, however, it would be impossible to understand the origin of the cavities in the altered crystals. The carbonate of baryta being more or less soluble, there can be no doubt that it has partially been removed by the waters through the medium of which the alteration was effected.

It might almost be conjectured what the ingredients contained in the water which comes into contact with the witherite are that have given rise to the alteration. One would naturally expect that sulphate of lime, held in solution in water, would convert the carbonate of baryta into sulphate of baryta. With a view to determine this, I poured into a vessel containing 100 grains of artificially prepared carbonate of baryta, 9292 grains of solution of gypsum in water, and allowed the fluid to stand for four days. This solution having being saturated, it must have contained 20 grains of sulphate of lime. It was then filtered, and the mass, collected upon the filter, washed with the greatest care. The residue, when treated with hydrochloric acid, was only partially dissolved, and this with effervescence. The portion which remained undissolved by the hydrochloric acid, weighed 15.41 grains, and consisted of sulphate of baryta which had been formed by the decomposition of the carbonate of baryta by the gypsum. The solution yielded on addition of sulphuric acid 97.79 grains of sulphate of baryta. The 15.41 grains of sulphate of baryta required for their formation 9.06 grains of sulphate of lime, and 13.034 of carbonate of baryta; while at the same time there must have been formed 6.684 grains of carbonate of lime. The sulphate of lime, which was decomposed, amounted therefore to scarcely one-half of the quantity present in the original solution. Oxalate of ammonia, when added to the fluid which contained the undecomposed sulphate of lime, occasioned a very perceptible turbidity. The 97.79 grains of sulphate of baryta indicate 82.77 grains of carbonate of baryta; when to this are added the 13.034 grains of carbonate of baryta, we obtain 95.751 grains, which deducted from the entire quantity, 100 grains employed, leave 4.249 grains. This quantity of carbonate of baryta

had been dissolved by the water of the gypsum solution and that employed in washing the residue. Carbonate of baryta being soluble in 4300 of its weight of water, the water in the solution of gypsum must have dissolved 2·156 grains of carbonate of baryta, and the water employed in washing, 2·093 grains. Hence—

100 grs. carbonate of baryta	}	quantities employed.
20 grs. sulphate of lime		
<hr/>		
120 grains.		

After decomposition—

	grains.
Sulphate of baryta - - -	15·41
Undecomposed carbonate of baryta -	82·717
Sulphate of lime in fluid filtered from these	10·94
Carbonate of baryta dissolved by the water	4·249
Carbonate of lime formed - -	6·684
	<hr/>
	120,000

If from these results an inference be drawn in regard to what takes place in nature, it may be supposed with the greatest probability that the conversion of carbonate into sulphate of baryta, described by Haidinger and Blum, has taken place in a similar manner.

When water containing gypsum continued to flow over witherite for a long period, sulphate of baryta and carbonate of lime were formed, which took up the place of the decomposed carbonate of baryta. The water in which the gypsum was brought, dissolved and removed a portion of the witherite. The circulation of the water went on certainly as slowly it does during the formation of stalactites in cavities in limestone; probably more slowly if the minerals undergoing alteration were inclosed in drusic cavities: so that an interval of several hours, or even days, may have elapsed between the falling of two successive drops. The length of time during which the drops of water remained in contact with substances, afforded them an opportunity of fully depositing such of the ingredients held in solution as took part in the process of alteration, and on the other hand of saturating themselves with new matter.

Supposing the gypsum solution, by which the witherite was converted into heavy-spar, to have been saturated, it must have contained  $\frac{1}{461}$  its volume of gypsum. If not merely a portion of this salt, as was the case in the above experiment, but the whole mass of the same had been consumed in the decomposition of the carbonate of baryta, which might well have been the case, the water remaining so long in contact with the witherite, it must have



become saturated with the latter, taking up therefore  $\frac{1}{4300}$  of it. If, for example, one part of witherite was gradually brought into contact with as much solution of gypsum as was sufficient to decompose it completely, there would be required for this purpose 0.695 part of sulphate of lime dissolved in 321 parts of water. This quantity of water, however, dissolves 0.0745 of carbonate of baryta, and would remove it without its undergoing decomposition. It remains, therefore, to determine how much of the witherite is decomposed, and how much is dissolved and carried away undecomposed.

If  $x$  represent the quantity of water which brings the gypsum required for the decomposition of the witherite, and which likewise dissolves and removes a corresponding quantity of the latter, we have  $\frac{x}{4300}$  the quantity of witherite dissolved, and 4300 that of the witherite decomposed. The quantity of gypsum required for the decomposition is  $0.695 \left(1 - \frac{n}{4300}\right) = 0.695 - \frac{0.695n}{4300}$ . Since now one part of gypsum is dissolved in 461 parts of water,  $0.695 - \frac{0.695n}{4300}$  gypsum is dissolved in  $\left(0.695 - \frac{0.695n}{4300}\right) 461$  parts of water. We have, therefore, the equation  $\left(0.695 - \frac{0.695n}{4300}\right) 461 = n$ . Consequently,  $n = 298$ , the quantity of gypsum required to effect the decomposition,  $= \frac{298}{461} = 0.646$ ; and the witherite which is dissolved and removed,  $\frac{298}{4300} = 0.069$ . Lastly, 0.646 of gypsum and one part of witherite by mutual decomposition yield 0.477 of calcspar and 1.099 baryta-spar. We have, therefore,—

Before decomposition.

1.000 part witherite.  
0.646 parts gypsum.

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1.646

After decomposition.

Baryta-spar	....	....	1.099
Calcspar	....	....	0.477
Undecomposed witherite,			
removed by water	....	....	0.069

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1.645

Had the alteration taken place in nature in this way, an increase in the mass must also have taken place. If, however, the gypsum solution which came into contact with the witherite was not a saturated, but a very diluted solution, the quantity of the witherite which was dissolved and removed by the water would be greater, while the quantity decomposed would be less. Should also the gypsum solution have contained free carbonic acid, the solvent capacity of the water for the carbonate of baryta would have been augmented, and a still larger portion of that salt would have been dissolved and removed.

The circumstance that Haidinger found in the baryta-spar

crystals many cavities filled with brown crystals of calcspar, renders it highly probable that the conversion of witherite into heavy-spar has actually taken place through the medium of water holding sulphate of lime in solution. The brown appearance of the crystals of calcspar indicates the presence of iron in the water; and this again, since iron occurs in water chiefly as carbonate, indicates the presence of free carbonic acid. Lastly, it must be further borne in mind that it all depends on the length of time during which the water containing gypsum remains in contact with the witherite, and whether all the gypsum undergoes decomposition or not. The decomposition of the witherite by gypsum is a process which, like all other decompositions of difficultly soluble bodies, does not take place instantaneously, but requires time. This was shown in the above-mentioned experiment. In nature, therefore, a greater or smaller amount of the gypsum will be removed undecomposed, should the drops of water in which it is held in solution fall upon the witherite too rapidly to allow a complete decomposition to ensue. If at the same time carbonate of baryta is dissolved, it is not decomposed by the gypsum until the fluid has already left the place where it came in contact with the witherite. This was likewise observed in the above experiments; for when the gypsum solution was, after four days, filtered from the residue, the filtrate appeared quite clear. After twenty-four hours, however, it became turbid, a crust at the same time forming upon its surface, which, by and by, sank to the bottom and was succeeded by a new crust. The crusts consisted for the most part of carbonate of lime, with a very small quantity of sulphate of baryta. The deposition of these crusts was still observed after an interval of nine days.

Water in which gypsum was present, having come in contact with witherite, and having given rise, by the mutual decomposition of the gypsum and witherite, to the formation of carbonate of lime and sulphate of baryta, would, when it had passed from the cavities in which this decomposition had taken place, into another quarter, where it lingered for a considerable time, have deposited calc-spar which it had carried away in solution. Seeing that the filtrate in the above experiment continued after a lapse of nine days to deposit traces of sulphate of baryta which had been formed by the subsequent decomposition of the dissolved carbonate of baryta by means of sulphate of lime, it may be seen how the water flowing into another empty space may there deposit, in addition to calcspar, a small quantity of baryta-spar also.

In this way the alteration of the witherite into sulphate of baryta may be, without any difficulty, conceived to be a decomposition of the former by water containing gypsum. Lastly, that carbonate of baryta may also have been converted into heavy-spar by water which contained sulphates of the alkalies or sulphate of magnesia, is self-evident.

An alteration similar to that above mentioned has been also undergone by baryto-calcite.\* Crystals of this mineral are sometimes seen, surrounded with an incrustation composed of crystals of heavy-spar: frequently, also, the incrustation consists entirely of a granular aggregate of small crystals of that mineral. According to Blum†, the crystals of the baryto-calcite become surrounded, in the first instance, with a crust of impure baryta-spar, which is easily separated, and beneath which appears the original crystal, no longer, however, presenting plane surfaces, sharp margins, and pointed corners, but more or less rounded, as if it had been exposed to the action of some solvent. The incrustation now increases somewhat in thickness; the baryto-calcite at the same time losing more and more substance, until at length it completely disappears, and hollow crystals of heavy-spar, in the form of the crystals of baryto-calcite, are left. The walls of these crystals are more or less drusy on their inner surface, and are composed of a very fine aggregate of sulphate of baryta. In the above alteration, the carbonate of lime is entirely removed, and to this Blum correctly attributes the hollow character of the crystals.

Sulphate of baryta, when boiled in a solution of carbonates of the alkalies, is to a certain extent decomposed, sulphates of the alkalies and carbonate of baryta being formed. At the ordinary temperature, the affinities are reversed, carbonate of baryta decomposing sulphates of the alkalies, while sulphate of baryta and carbonates of the alkalies are formed.

It was to be expected that, since these two very opposite actions depended on a difference of temperature, there would be an intermediate point at which neither the sulphate of baryta is decomposed by carbonates of the alkalies, nor carbonate of baryta by sulphates of the alkalis. With a view to ascertain this, six solutions of carbonate of potash were prepared, each containing 60 grains of the salt dissolved in 1500 grains of water. To each of the solutions were added 100 grains of sulphate of baryta. One of the solutions was boiled for half-an-hour, the others were exposed for

\* Haidinger, loc. cit.

† Loc. cit. p. 47.

the same length of time to the respective temperatures mentioned below.\* They were then filtered, and thoroughly washed,—still at the same temperature. In the first three, the quantity of the sulphate of baryta which remained undecomposed was determined quantitatively, in the others this could not be done, inasmuch as the fluid passed in a state of turbidity through the filter. Moreover, the decomposition in these was so slight as to be recognized only by means of reagents; this, however, was sufficient for the object in view.

Experiment.	Temperature F. degrees.	Sulphate of baryta decomposd. per cent.
1	219 — 221	17·06
2	167 — 171	2·15
3	145 — 149	1·63
4	122 — 126	...
5	100 — 104	...
6	77 — 81	...

That decomposition had taken place in the three latter experiments, was shown from the circumstance that the filtrate, although it was already turbid, became still more so on addition of chloride of barium, and consequently contained sulphate of potash. In like manner hydrochloric acid, with which the remaining sulphate of baryta was treated, became turbid on addition of sulphuric acid, thus indicating the presence of carbonate of baryta. The filtrate in the first experiment became turbid on cooling, because it contained, besides sulphate of potash, some dissolved carbonate of baryta, which two salts decomposed each other when the temperature decreased. The point of indifference, therefore, still lies beneath 77°—81° F.

In nature no such concentrated solutions of carbonate of potash probably ever occur: the following experiments were made, therefore, in order to ascertain the decrease in the amount of sulphate of baryta decomposed, with increase in the dilution of the carbonate of potash solution. Solutions were prepared, each containing 60 grains of carbonate of potash dissolved in different quantities of water, and to each of these, 100 grains of sulphate of baryta were added. They were boiled for half-an-hour.

\* Since these experiments were intended to imitate similar processes possibly occurring in nature, the pulverised baryta-spar, in being heated with the solution of carbonate of potash, was not disturbed in any way. In the first experiment, the motion caused in the baryta-spar by the boiling could not, of course, be prevented.



Experiment.	Dilution.	Sulphate of baryta decomposed.
7	... 25 times as much water as carbonate of potash.	... 17.06 per cent.
7	... 200	... 8.13
8	... 400	... 5.47
9	... 800	... 4.06

It is to be observed, that with dilution of the carbonate of potash solution, the amount of sulphate of baryta which is decomposed diminishes but very gradually.

The more the solution of the carbonate of potash is diluted, the more of the carbonate of baryta arising from the decomposition of the sulphate of baryta is dissolved. If 4,300 parts of water are present for every part of carbonate of baryta formed in this way, this is sufficient to dissolve it. The entire quantity of the carbonate of baryta is always removed by the water when the latter amounts to 4,300 times as much as the former, or more.

It deserves to be noticed, that Senarmont,\* upon inclosing freshly precipitated sulphate of baryta along with a solution of bicarbonate of soda in a glass tube, and exposing it to a temperature of 250° C. for 60 hours, observed on the walls of the tube microscopic crystals having the form of those of baryta-spar. It may be conceived that at so high a temperature, and continued so long, a much greater quantity of sulphate of baryta was decomposed, which again formed when the temperature decreased. He obtained the same result by treating sulphate of baryta in the way above mentioned with diluted hydrochloric acid. The latter experiment, however, has no interest in a geological point of view, there being no grounds for supposing that in the mineral kingdom hydrochloric acid acts as a solvent of heavy-spar.

Alkaline carbonates, especially carbonate of soda, occur very frequently in springs, and not seldom in large quantities. Baryta salts, on the other hand, are present only in few springs; the accuracy of the older analyses, in which these salts are mentioned, must therefore be doubted. Carbonate of baryta occurs, according to Planiana, in the mineral water at Luhatschowitz; and sulphate of baryta, according to Brandes, in the mineral springs of Pyrmont and Meinberg. According to my analyses, there seems to be a trace of baryta in the mineral spring at Lampheid. Hunt† states that in two cold mineral springs at Varennes there are 0.012 and 0.023 parts of carbonate of baryta; and in a mineral spring at

\* Ann. de Chim. et de Phys. (3) Vol. 32, p. 129.

† Silliman, American Journ. (2) Vol. 11, p. 174.

St. Leon, in Canada, 0·002 of chloride of barium per 1000 parts of water. Fresenius\* found in the water of the Kochbrunnen, at Wiesbaden, a trace of carbonate of baryta; he confirms the observation of Struve, as to the presence of carbonate of baryta in the Kränchen, and he found this carbonate in the other warm springs of Ems also. All these springs likewise contain carbonate of strontia. These two carbonates amount together to 0·0012—0·004 per 100 parts of water. The presence of carbonate of baryta in these springs is the less to be doubted, seeing that baryta salts are found in still greater proportions in the deposits which take place from them (p. 150). It was already remarked, that in the water of the Kesselbrunnen the bicarbonate of baryta cannot remain long in solution, owing to the presence of sulphate of soda. There can be no doubt, therefore, that in this water, which has a temperature of 116° F., these two salts, when the temperature falls, give rise by mutual decomposition to the formation of sulphate of baryta. Fresenius is inclined to ascribe the opalescent character which this water presents when left in closed vessels during the night, to the sulphate of baryta so formed. This view is supported by the fact, that on addition of hydrochloric acid, the opalescence does not immediately disappear, but only when the water has been shaken for some time. The separation of sulphate of baryta, therefore, from warm springs containing carbonate of baryta and sulphates of the alkalies, which I had already shown by researches mentioned in the German edition† of the present work, must necessarily take place, has been fully confirmed by the subsequent analyses of Fresenius.

Seeing that, the warm springs at Ems and Wiesbaden may upon reaching the surface, and where in consequence their temperature falls, deposit sulphate of baryta along with other mineral substances, it may be supposed that in former periods also, similar ascending warm springs, especially those which contained only carbonate of baryta and sulphates of the alkalies, have deposited sulphate of baryta only, and removed the alkaline carbonates. In this way the formation of beds of heavy-spar, (p. 433) may be explained quite simply.

The occurrence of heavy-spar in fissures, however, cannot be explained by supposing that it has been deposited from warm springs which passed up through such fissures. The ascent of such waters takes place too rapidly to allow any marked decrease of temperature to ensue; moreover, the channels of these springs

\* Annal. der Chemie. Vol. 82, p. 249.

† Vol. 1, p. 629

ave been long since warmed to such a degree, that the adjacent rock can no longer exercise any cooling influence. The only supposition which remains, therefore, is that ascending warm waters, which held in solution carbonate of baryta and sulphates of the alkalies, had, during their course upon the surface, trickled down the walls of fissures, and deposited on cooling sulphate of baryta.

It has, moreover, been already shown (p. 141) that deposits cannot be conceived to take place from ascending springs during their ascent.

Whilst, according to kind communications I have received from Monsieur Göttl, an apothecary in Carlsbad, the foundation for a building was being lately dug in the granite of that place, a hot spring appeared bursting out from fissures. Upon the granite of one of these fissures there were found projecting crystals in considerable numbers. Since the crystalline form left some doubt remaining as to whether the crystals were actually heavy-spar, I analyzed one of them, and in this way removed the doubt. Strontia, which occurs in the hot springs of Carlsbad, I could not find in the crystal in question; it might be conjectured that this sulphate of baryta has been deposited from the hot waters, because previous to the digging they could not come to the surface, and must, therefore, have been stagnant. I will not, however, venture to speak decidedly on the point; this occurrence of baryta-spar is nevertheless remarkable.

Göttl took occasion to examine the hot springs of Carlsbad with a view to baryta: a great quantity of the precipitate which is obtained during the preparation of the Carlsbad salts was dissolved in hydrochloric acid. When to a portion of this solution sulphuric acid was added, and to another portion a solution of sulphate of lime, minute precipitates were produced, which consisted of sulphate of baryta and sulphate of strontia, and by means of the blowpipe the presence of chromium was also ascertained.

The analyses of two brines on the Alleghany river (p. 377) and the analysis above cited, of a mineral spring at St. Leon, point out chloride of barium. I know of no other mineral-spring in which this salt of barium has been found. No certain conclusions can be drawn from such rare cases. Should this salt, however, have occurred in springs more frequently in earlier times, it would be less difficult to explain the deposition of sulphate of baryta, seeing that sulphates are by no means rare in springs. Nevertheless, here, as in all cases where we are induced to assume a removal of sulphate of baryta by means of water, we are opposed

by the great difficulty of solubility of this salt. If the Plutonists make use of this circumstance to combat our view, we reply that their view, that the introduction of the sulphate of baryta in the melted state into fissures, is met by an equally great objection, the extraordinary difficulty with which this salt is fused. For us, however, there remains a way of escape, in the fact that insolubility of a body is never to be understood in the absolute sense. With whatever difficulty, therefore, solution may be effected, we require only water and time in order to be able to comprehend how a removal of it may take place. If we have recourse to the two great geological aids just mentioned, we cannot imagine any objection against the introduction of sulphate of baryta by pure water.

According to Klaproth, the sulphate of baryta dissolves in 43,000 parts of water.\* Seeing, however, that a solution of one part of chloride of barium in 200,000 parts of water is, after some time, rendered more or less turbid by sulphuric acid, and the sulphate of baryta so produced amounts to  $\frac{1}{209424}$  of the fluid, it must require more than 209,424 times the quantity of water for its solution. The above estimate is, therefore, certainly incorrect. In every instance, therefore, great quantities of water, and long intervals of time, are required before a crystal of baryta-spar of only moderate size can be dissolved and removed by water.

We still set it down as possible, that waters may contain sulphuret of barium in solution, and that this, during its deposition, is oxidised and converted into sulphate of baryta. It might at least be imagined, that the solution and removal of crystals of heavy-spar, as the pseudomorphs in forms of this spar pre-suppose, would have been facilitated by a minute proportion of organic substances, which are rarely wanting in waters, the very difficultly soluble sulphate of baryta being, by means of these, gradually converted into the easily soluble sulphuret of barium.

#### D.—*Cölestine*

Hitherto, this mineral has not, any more than heavy-spar, been found as a mineralogically definable constituent of crystalline rocks. Cölestine occurs in metalliferous veins in gneiss, mica slate and clay slate, in drusic cavities, in marl of muschelkalk, in the limestone and marl of different formations, frequently associated with gypsum and sulphur, in sandstone, in fissures in flint, in brown

\* Hiersford (Silliman's American Journal, Vol. 9, p. 176) gives the same number, merely, however, on the authority of Klaproth, not from any researches of his own.



coal, and in drusic cavities in amygdaloids.\* All these localities, as well as its occurring as a lapidifying agent in ampullariæ, echnites, ammonites, &c., speak decisively for its formation in the wet way. Traces of sulphate of strontia are also frequently found in heavy-spar; and in the baryto-sulphate of strontia, which occurs in great quantity on Drummound Island in Lake Erie, and at Kingston in Upper Canada, strontia is the predominating constituent. Dykes, completely filled with cölestine, are not found; in this respect it differs from heavy-spar. Alteration or displacement pseudo-morphs of cölestine are unknown.

Deposits of sulphate of strontia from waters are much more easily understood than those of heavy-spar, seeing that the former salt is much more easily soluble than the latter; it requires only 3600 parts of boiling water, and remains dissolved after cooling.†

It is by no means rare to find that in the analysis of mineral waters the lime which separates shows traces of strontia. Berzelius was the first who discovered it in the hot springs of Carlsbad. It was afterwards detected in the other Bohemian mineral waters, that of Teplitz excepted. Its presence was also pointed out in the mineral springs at Salzbrunn, Aix-la-Chapelle, Burtscheid, Pyrmont, Meinberg, in the Alexisbrunnen and in the Silkenbrunnen. Out of 35 mineral springs in the environs of the Laacher See, the analysis of which I have communicated in the German edition of this work,‡ 17 showed more or less appreciable traces of strontia. In the warm springs at Ems this earth exists in such proportions as to admit of being determined quantitatively (p. 150). From these facts it may be seen that in rocks strontia must be pretty generally distributed, although only in very minute quantities.§

In the basalt of Stetten, in the Hügau, C. Gmelin|| found 0.112,

\* Blum, Nachtrag zu den Pseudomorphosen, p. 177.

† Against that Presenius found that it requires 6395 parts of cold, and 9638 of boiling water (Annalen der Chemie, Vol. 69, p. 122.)

‡ Vol. 1, p. 357, fol.

§ It is remarkable that in springs strontia is found so frequently; baryta, on the other hand, so rarely; whilst again the deposits of sulphate of baryta occur in general in far greater quantities than those of sulphate of strontia. When we reflect, however, that the examination of the carbonate of lime, which separates in the analysis of spring water, for strontia, by the reddening of the alcohol flame, is, even when only minute traces are present, much easier than the examination for baryta, and is on this account seldom neglected, we must not, from such analyses, without any further ground, conclude that in water baryta occurs much more rarely than strontia.

|| This is  $\frac{1}{108}$  of the lime contained in this basalt. According to Berzelius, the strontia in the sprudel of Carlsbad amounts to only  $\frac{1}{321}$  of the lime contained in the same.

and in the basalt of Engelhaus, near Carlsbad, Rammelsberg\* found 0.04% of strontia. In carbonate of lime extracted by a feeble acid from a melaphyr, I detected very distinctly the presence of this earth, but not in the silicate of lime of the same rock. In an amygdaloid from Idar, however, as well as in a calcspar from a druse in a rock, I found very appreciable traces of strontia. A highly decayed rock (gaboornite hypersthene), which occupies a fissure in the clay-slate below Boppard, on the Rhine, exhibited very feeble but nevertheless appreciable traces. Calcspar, which fills a fissure in this rock six inches in width, and which has no doubt been extracted by waters from the rock, inasmuch as this effervesces very strongly with acids, exhibited very distinct traces of strontia. In both cases, therefore, strontia must occur in the adjacent rocks just as in their fissures or in their drusic cavities. Two specimens of calcspar, the one from a druse in the basalt of the Minderberg, the other from a fragment of basalt at Leubsdorf, above Luiz, where the intervals between the columns of basalt are quite filled with carbonate of lime contained in like manner, particularly the latter, very appreciable traces of strontia. So also Stromeyer found arragonite, containing strontia, in drusic cavities and in clefts in basalt from the Blaue Kuppe at Eschwege, from Aussig, from Watsch in Bohemia, and in dolerite from the Kaiserstuhl. It is clear that the materials for the formations in drusic cavities can only come from the adjacent rocks, for all that is contained in such cavities has been extracted from the surrounding rocks by the percolating waters. Strontia must therefore be by no means a rare, although certainly a very minute constituent of basaltic rocks;† no doubt it is, like the lime, present as silicate in basalt, perhaps in its labradorite, and is afterwards converted by carbonic acid into a bicarbonate, in which combination it occurs in springs. Since, however, the carbonate of strontia is soluble in 1536 parts of boiling, and in a greater quantity of cold water,‡ it may in nature be dissolved even by water containing no carbonic acid. Although the strontia in mineral springs may very well be

\* Handwörterbuch, &c. Suppl. 4, p. 16.

† In the analysis of other rocks or minerals containing silicate of lime, strontia would, if attention were directed to it, be found, no doubt, as frequently as in mineral spring water. Since, however, this earth seems to occur always in only very minute quantities, and is, during the analysis, precipitated along with the lime by oxalate of ammonia, it easily escapes the notice of the chemist, unless he examines this precipitate. In washing the same, the oxalate of strontia may, moreover, be readily washed away, seeing that it is soluble in 1920 parts of boiling water.

‡ Fresenius (loc. cit.) found that it requires 18,045 parts of cold water.

conceived to be a product of decomposition of sulphate of strontia, seeing that most of the springs above mentioned contain carbonate of soda, yet in regard to the strontia in the other localities in which it is found, such a decomposition is less probable. The calcspar in drusic cavities in basalt, &c., is no doubt a deposit from water which passes from above downwards through such rocks. This water contains in general no alkaline carbonates; it decomposes, by means of its free carbonic acid, the silicates of lime in the rocks, and deposits the dissolved carbonate of lime in drusic cavities. It is in the highest degree probable that the same thing happens in regard to the minute quantities of carbonate of strontia which accompany the carbonate of lime.

Upon fusing a mixture of felspathic porphyry and sulphate of strontia, I found that the latter was not decomposed by the alkaline silicates of the former. Hence in volcanic rocks sulphate of strontia may be conceived to exist in the undecomposed state.

The silicate of strontia has not as yet been examined. We know only that 1 part of silicic acid fused along with 2 parts of strontia is decomposed by acids. I prepared this combination by decomposing nitrate of strontia with silicate of soda, and washing the precipitate thoroughly. The latter salt was obtained by saturating a solution of soda with silicic acid prepared by passing fluosilicic gas through water, and very carefully washed. Already during the washing of the silicate of strontia, I remarked that, like the silicate of baryta, it is pretty soluble in water. I found that 1 part requires for its solution 996 parts of boiling, or 1262 parts of cold water. It was composed of 2 equivalents of silicic acid, 2 equivalents of strontia, and 3 equivalents of water.

In order to ascertain the behaviour of this silicate of strontia with soluble sulphates, it was dissolved in boiling water, the solution divided into four portions, and the four salts: —1, sulphate of soda; 2, sulphate of potash; 3, sulphate of lime; and 4, sulphate of magnesia, added in aqueous solutions. None of these solutions were troubled, and even after 24 hours, that containing the sulphate of soda exhibited no turbidity; from the solutions with sulphate of potash and sulphate of magnesia, on the other hand, a few flakes of silicate of strontia had separated during the cooling of the solutions. The solution with sulphate of lime had become very turbid without separation of flakes. The silicate of strontia and sulphate of lime had, therefore, decomposed each other into silicate of lime and sulphate of strontia, as was to be anticipated, seeing that

the two latter salts are much more difficultly soluble than the former.

Between the silicate of strontia and the other sulphates mutual decompositions must also be expected, since the sulphate of strontia is much more difficultly soluble than the silicate, requiring three times as much water as the latter. The circumstance that the solution of silicate of strontia remained clear on the addition of concentrated solutions of the two alkaline sulphates, is therefore a phenomenon difficult of explanation; still more difficult is it to explain why on bringing together the solutions of silicate of strontia and sulphate of magnesia no turbidity ensued, although the silicate of magnesia is a difficultly soluble salt. That the solution of the silicate of strontia had actually decomposed the alkaline sulphates, was shown by the weakly alkaline reaction of the fluid. This could be observed more distinctly when a solution of sulphate of soda was poured over silicate of strontia and a gentle heat applied; reddened litmus paper became blue in the fluid. There had been formed, therefore, silicate of soda, which, like all soluble silicates, exhibited an alkaline reaction. The behaviour of silicate of strontia with sulphate of magnesia is probably the same, only it is ascertained with more difficulty.

From these experiments it is seen that the silicate of strontia behaves with soluble sulphates in the same manner as the silicate of baryta; that, namely, a mutual decomposition takes place. Whether this decomposition is complete, as in the case of the silicate of baryta, remains to be ascertained. It also follows from these experiments, that sulphate of strontia can exist in a solution in presence of silicates of the alkalies, silicate of lime, or probably also of silicate of magnesia.

A decomposition of the carbonate of strontia by alkaline sulphates, at ordinary temperatures, as is the case with the carbonate of baryta, was not to be expected, since sulphate of strontia is a soluble, although a difficultly soluble, salt, in presence of which alkaline carbonates cannot exist. I examined, however, whether perhaps an alkaline reaction might be exhibited when carbonate of strontia is treated with a solution of an alkaline sulphate. Slightly reddened litmus paper became, in fact, blue; only a closer examination showed that carbonate of strontia itself has an alkaline reaction. This hitherto unobserved alkaline reaction of this carbonate stands no doubt in connection with its pretty easy solubility in water.



If the waters, which extract sulphate of strontia out of the rocks, contain alkaline carbonates, or if they become impregnated therewith in the rocks by decomposing alkaline silicates, carbonate of strontia is formed, which, on account of its being pretty easily soluble, may be readily removed and deposited in fissures, &c. In this way, therefore, the occurrence of strontianite may be easily understood.

END OF VOL. I.



